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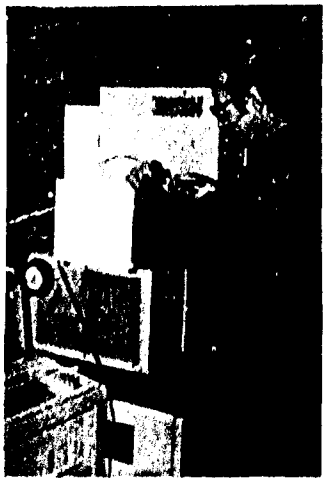

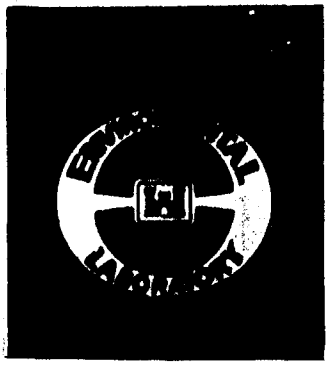

WATER QUALITY RESEARCH PROGRAM

TECHNICAL REPORT EL-89-18

QUALITY ASSURANCE GUIDELINES FOR ORGANIC ANALYSIS

by

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Environmental Laboratory

DEPARTMENT OF THE ARMY
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December 1989
Final Report

Approved For Public Release; Distribution Unlimited

Prepared for DEPARTMENT OF THE ARMY
US Army Corps of Engineers
Washington, DC 20314-1000

Under WQRP Work Unit 31766

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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report EL-89-18	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION USAEWES Environmental Laboratory 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) 3909 Halls Ferry Road Vicksburg, MS 39180-6199	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION US Army Corps of Engineers 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) Washington, DC 20314-1000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO. 31766
11. TITLE (Include Security Classification) Quality Assurance Guidelines for Organic Analysis	
12. PERSONAL AUTHOR(S) Karn, Richard A.; Strong, Ann B.	
13a. TYPE OF REPORT Final report 13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) December 1989 15. PAGE COUNT 84
16. SUPPLEMENTARY NOTATION Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.	
17. COSATI CODES FIELD / GROUP / SUB-GROUP	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Environmental regulatory methods, Quality control, Organic analysis, Quality assurance guidelines.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The US Army Corps of Engineers has a fundamental responsibility to produce analytical data that are precise and accurate and meet environmental regulations imposed by the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Recovery Act, the Superfund Amendments and Reauthorization Act, the Safe Drinking Water Act, and the Toxic Substances Control Act. Numerous analytical methods for organic analysis are promulgated to provide the same basic information with only slight variations in procedure. This report was written to provide general quality assurance guidelines for organic analysis with specific quality assurance/quality control requirements for the various methods. Keywords:

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

PREFACE

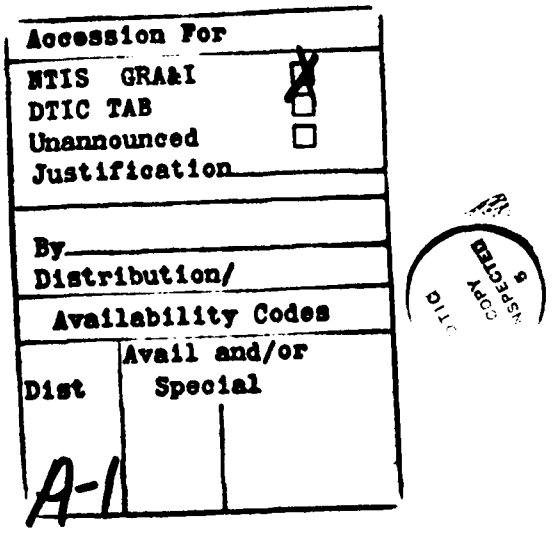
This study was conducted by the US Army Engineer Waterways Experiment Station (WES), Environmental Laboratory (EL), Vicksburg, MS. Funds were provided through Work Unit 31766 of the Water Quality Research Program (WQRP), which is sponsored by the Headquarters, US Army Corps of Engineers (HQUSACE). The WQRP is managed within EL's Environmental Resources Research and Assistance Programs (ERRAP). Mr. J. Lewis Decell is the ERRAP Program Manager. The HQUSACE Technical Monitor for WQRP was Mr. Dave Buelow.

This report was prepared by Mr. Richard A. Karn and Ms. Ann B. Strong of the Analytical Laboratory Group, Environmental Engineering Division (EED), EL. The work was conducted under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Chief, EL. This report was edited by Ms. Lee T. Byrne of the Information Technology Laboratory.

COL Larry B. Fulton, EN, was Commander and Director of WES. Dr. Robert W. Whalin was Technical Director.

This report should be cited as follows:

Karn, Richard A., and Strong, Ann B. 1989. "Quality Assurance Guidelines for Organic Analysis" Technical Report EL-89-18, US Army Engineer Waterways Experiment Station, Vicksburg, MS.



CONTENTS

CONVERSION FACTORS, NON-SI TO SI (METRIC) UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
feet	0.3048	metres
gallons (US liquid)	3.7854	litres
inches	25.4	millimetres
quarts (US liquid)	0.9463	litres
ounces (US fluid)	0.02957353	cubic decimetres

QUALITY ASSURANCE GUIDELINES FOR ORGANIC ANALYSES

PART I: INTRODUCTION

Background

1. The US Army Corps of Engineers (CE) is involved with numerous projects that are subject to environmental regulations including the Clean Water Act (CWA); the Resource Conservation and Recovery Act (RCRA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); the Superfund Amendments and Reauthorization Act (SARA); the Safe Drinking Water Act (SDWA); and the Toxic Substances Control Act (TSCA). To meet the monitoring requirements of these regulations, a number of analytical procedures are used to assess the organic contaminants in environmental samples. Most of the procedures are approved by the US Environmental Protection Agency (USEPA), the American Society for Testing and Materials (ASTM), or the US Geological Survey (USGS). Procedures requiring gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) are the most frequently used techniques. Many of the procedures are similar, varying only slightly in sample preparation or quality assurance/quality control (QA/QC) measures. This report summarizes the most commonly used organic analysis procedures and reference sources. The report also provides QA/QC guidance to CE personnel who either perform organic chemical analyses or monitor contractor laboratories.

Purpose

2. The purpose of this study is to provide CE personnel with a ready reference to the QA/QC needed to adequately conduct and evaluate environmental studies involving organic chemical analyses.

Approach

3. In this report, the sequence of events involved with sample analysis is presented from sample handling in the field to the final reporting of data. Quality assurance/quality control procedures are recommended for every step in

the analytical process. Sampling plans, with respect to numbers of samples, site locations, and sampling procedures are beyond the scope of this report.

Definitions

4. Definitions used in this report are listed in the following:

   a. Accuracy. Accuracy refers to the agreement between the measured value and the true value. It is usually assessed by analyzing reference samples or spiked samples.

   b. Blank. Blanks are used to determine the introduction of contaminants into the analytical process. Trip blanks consist of reagent water carried to the field in sealed containers and transported back to the laboratory. Reagent blanks or method blanks are aliquots of reagent water carried through the laboratory analytical process.

   c. Internal standard. Internal standards are compounds that are similar in analytical behavior to the compounds of interest, yet will not interfere with the sample matrix. They are added to sample extracts just prior to injection into the GC or GC/MS.

   d. Matrix spike. Actual samples are spiked with known quantities of certain analytes prior to sample extraction/digestion and are used to determine percent recoveries.

   e. Precision. Precision refers to the agreement between duplicate or replicate analysis.

   f. Reference sample. A reference sample usually refers to a sample that is of similar matrix to samples being analyzed and contains known quantities of the analytes of interest.

   g. Surrogate. Surrogates are compounds that are similar to the analytes of interest but are not normally found in environmental samples. They are spiked into blanks, standards, samples, and spiked samples, prior to analysis. Percent recoveries are calculated for each surrogate.

PART II: SAMPLE COLLECTION AND HANDLING

5. Sample collection introduces one of the largest sources of error in the analytical process and is probably the least controlled. The aim of sampling is to obtain a representative portion of the environment to adequately characterize its components. After the sample is collected, it must be handled properly to maintain the integrity of the sample. Part II of this report deals with sample containers, preservation, and shipment.

Sample Containers

6. Samples for organic analysis are almost always collected in glass containers with Teflon-lined lids to eliminate interferences from plasticizers and to reduce adsorption of organics on container walls. This is particularly important when trace levels are being identified and quantified.

Volatile organic compounds

7. Water samples are usually collected in 40-ml glass volatile organic analysis (VOA) vials with Teflon-lined septum caps. Precleaned vials are available commercially, or they may be cleaned by washing with soap and water, followed by a distilled deionized water rinse. They should then be placed in a muffle furnace and heated at 105° C for approximately 1 hr. Soil or sediment samples may also be collected in the 40-ml vials, but they are easier to handle in 4- or 8-oz* wide-mouth glass jars with Teflon-lined lids.

Semivolatile organics

8. Semivolatile organics include pesticides, herbicides, polychlorinated biphenyls (PCBs), and base-neutral/acid extractable compounds. Various sizes (1 qt to 2-1/2 gal) of glass bottles with Teflon-lined caps are used to collect water samples for these analyses. Amber-colored glass is preferred. Containers are scrupulously cleaned by soaking with soap and hot water, rinsing, soaking with oxidizing agent, hot-water rinsing, distilled-water rinsing, methanol rinsing, and rinsing with the solvent to be used in the analysis. Empty solvent bottles make suitable sample bottles. Wide-mouth glass bottles

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* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 3.

with Teflon-lined lids are used to collect soil/sediment samples. Precleaned bottles are also available commercially.

Handling and Preservation

9. Proper handling and preservation are essential to sample integrity. Samples for organic analysis are easily contaminated in the collection process. Recommendations for collection and transportation are as follows.

Volatile organics

10. Duplicate water samples are taken in the VOA vials from the same location. Rapid filling can cause loss of volatile compounds. Care is taken to be sure that the vials are completely filled with no air space. If air bubbles appear when the vials are inverted, they must be emptied and refilled. Care must be taken not to agitate the samples when the vials are filled so that loss of volatile compounds is reduced. Sample containers for soil and sediment samples should also be filled completely, keeping air space to a minimum. Each sample container should be sealed in a separate plastic bag for shipping. Because volatile organic compounds can migrate through the septums on the VOA vials, trip blanks consisting of distilled water are carried through the entire sample collection and shipping process. Sample bottles should not be filled near running motors or exhaust systems. Samples should be placed on ice with sufficient packing material to prevent breakage and should be shipped as soon as possible. Analysis for volatile organics should be performed within 14 days.

Semivolatile organics

11. Sample containers should be filled with care, avoiding direct contact of rubber gloves with the samples, and should not be filled in the presence of exhaust fumes. Soil or sediment samples collected with polyvinylchloride (PVC) coring devices should be removed from contact with the PVC as soon as possible. The outer portion of the sample should be removed with a scalpel or similar instrument, and the samples placed in glass jars and packed in ice for shipping. Sufficient packing material should be placed around the samples to prevent breakage. To meet USEPA criteria, samples should be extracted within 7 days after collection and analyzed within 40 days.

Chain-of-Custody

12. If samples are subject to litigation, they should be collected under chain-of-custody, a combination of good sample collection techniques and documentary evidence of procedures followed. Samples are considered to be in custody if they are:

a. In actual physical possession.

b. In view, after being in physical possession.

c. In physical possession and locked up.

d. In a designated secure area.

Written documentation should follow the sample from the time of collection to the time of analysis and final discard. Tamper-proof seals should be used on each sample or group of samples to ensure sample integrity. Each sample container should have a unique number or identity. A chain-of-custody form should accompany the samples showing the person, time, and date of each transfer of possession. Detailed procedures for chain-of-custody are given in USEPA (1982).

Sample Receipt at the Laboratory

13. Samples are checked at the laboratory to be sure that information contained on the transmission sheets correspond to the samples received. If samples are sent under chain-of-custody, seals are checked for sample integrity, and information on custody forms are checked against sample container information before signing. The samples in the ice chests should still be cool when received at the laboratory. Elevated temperatures can cause the loss of many organic compounds. Water samples for VOA should be checked to be sure that no air bubbles are present.

PART III: ANALYTICAL METHODS

14. Approved analytical methods to meet the various environmental regulations were taken from a number of sources and are presented according to regulatory statutes.

The CWA

15. Approved analytical methods for contaminants regulated by the CWA and pursuant to National Pollutant Discharge Elimination System permits are given in Tables 1 and 2 taken from the Federal Register, Vol 49, No. 209, Friday, 26 October 1984, 40 Code of Federal Regulations (CFR) Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act." All of the "600" series of methods are contained in this reference. Other methods are taken from Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA) (1984), and Annual Book of ASTM Standards, Vol 11, ASTM (1988).

The RCRA

16. The USEPA has recently promulgated (Federal Register 1989) mandatory adherence to the procedures and methods in Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (USEPA 1986b) for all RCRA testing. Table 3 summarizes the basic QC requirements for this testing. Additional specific QA/QC requirements are contained in each of the analysis methods from USEPA (1986b) cited in Table 4 for individual organic compounds.

The SDWA

17. The SDWA was amended in 1986 to require testing for numerous organic compounds not previously regulated or monitored under the National Primary Drinking Water Regulations (NPDWR). The approved methods of analysis presented in Table 5 were taken from Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Water (USEPA 1986a). This reference is currently undergoing revision. These methods are frequently referred to as the "500" series and are very similar to the "600" series used for the

Table 1

List of Approved Procedures for Nonpesticide Organic Compounds

Parameter	USEPA Method Number* GC	GC/MS	HPLC	Other**
Acenaphthene	610	625,1625	610	
Acenaphthalene	610	625,1625	610	
Acrolein	603	624,1624	--	
Acrylonitrile	603	624,1624	--	
Anthracene	610	625,1625	610	
Benzene	602	624,1624	--	
Benzidine	--	625,1625	605	p 1
Benzo(a)anthracene	610	625,1625	610	
Benzo(a)pyrene	610	625,1625	610	
Benzo(b)flouranthene	610	625,1625	610	
Benzo(ghi)perylene	610	625,1625	610	
Benzo(k)flouranthene	610	625,1625	610	
Benzyl Chloride		--	--	p 130
Benzyl Butyl Phthalate	606	625,1625	--	
Bis(2-chloroethoxy)methane	611	625,1625	--	
Bis(2-chloroethyl)ether	611	625,1625	--	
Bis(2-ethyl hexyl)phthalate	606	625,1625	--	
Bromodichloromethane	601	624,1624	--	
Bromoform	610	624,1624	--	
Bromomethane	610	624,1624	--	
4-Bromophenyl phenyl ether	601	624,1624	--	
Carbon tetrachloride	601	624,1624	--	p 130
4-chloro-3-methyl phenol	604	625,1625	--	
Chlorobenzene	601,602	624,1624	--	p 130
Chloroethane	601	624,1624	--	
2-Chloroethylvinyl ether	601	624,1624	--	
Chloroform	601	624,1624	--	p 130
Chloromethane	601	624,1624	--	
2-Chloronaphthalene	612	625,1625	--	
2-Chlorophenol	604	625,1625	--	
4-Chlorophenyl phenyl ether	611	625,1625	--	
Chrysene	610	625,1625	610	
Dibenzo(a,h)anthracene	610	625,1625	610	
Dibromchloromethane	601	624,1624	--	
1,2-Dichlorobenzene	601,602,612	624,625,1625	--	
1,3-Dichlorobenzene	601,602,612	624,625,1625	--	

(Continued)

Source: Federal Register (1984).

* The full texts of methods 601-613, 624, 625, 1624 and 1625 are given in 40 CFR, Appendix A, Part 136, "Test Procedures for Analysis of Organic Pollutants."

** USEPA, 1978 (Sep), "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater."

(Sheet 1 of 3)

Table 1 (Continued)

Parameter	USEPA Method Number GC	GC/MS	HPLC	Other
1,4-Dichlorobenzene	610,602,612	625,1624,1625	--	
3,3'-Dichlorobenzidine	--	625,1625	605	
Dichlorodifluoromethane	601	--	--	
1,1-Dichloroethane	601	624,1624	--	
1,2-Dichloroethane	601	624,1624	--	
1,1-Dichloroethene	601	624,1624	--	
trans-1,2-Dichloroethene	601	624,1624	--	
2,4-Dichlorophenol	604	625,1625	--	
1,2-Dichloropropane	601	624,1625	--	
cis-1,3-Dichloropropene	601	624,1624	--	
Trans-1,3-Dichloropropene	601	624,1624	--	
Diethyl phthalate	606	625,1625	--	
2,4-Dimethyl phenol	604	625,1625	--	
Dimethyl phthalate	606	625,1625	--	
Di-n-butyl phthalate	606	625,1625	--	
Di-n-octyl phthalate	606	625,1625	--	
2,4-Dinitrophenol	604	625,1625	--	
2,4-Dinitrotoluene	609	625,1625	--	
2,6-Dinitrotoluene	609	625,1625	--	
Epichlorohydrin	--	--	--	p 130
Ethylbenzene	602	624,1624	--	
Fluoranthene	610	625,1625	--	
Fluorene	610	625,1625	--	
Hexachlorobenzene	612	625,1625	--	
Hexachlorobutadiene	612	625,1625	--	
Hexachlorocyclopentadiene	612	625,1625	--	
Hexachloroethane	612	625,1625	--	
Indeno(1,2,3-cd)pyrene	610	625,1625	--	
Isophorone	609	625,1625	--	
Methylene chloride	601	624,1624	--	
2-Methyl-4,6-dinitrophenol	604	625,1625	--	
Naphthalene	610	625,1625	610	
Nitrobenzene	609	625,1625	--	
2-Nitrophenol	604	625,1625	--	p 130
4-Nitrophenol	604	625,1625	--	
N-Nitrosodimethylamine	607	625,1625	--	
N-Nitrosodi-n-propylamine	607	625,1625	--	
N-Nitrosodiphenylamine	607	625,1625	--	
2,2-Oxybis(1-chloropropane)	611	625,1625	--	
PCB-1016	608	625	--	p 43
PCB-1221	608	625	--	p 43
PCB-1232	608	625	--	p 43
PCB-1242	608	625	--	p 43
PCB-1248	608	625	--	p 43
PCB-1254	608	625	--	p 43

(Continued)

Table 1 (Concluded)

Parameter	USEPA Method Number GC	GC/MS	HPLC	Other
PCB-1260	608	625	--	p 43
Pentachlorophenol	604	625,1625	--	p 140
Phenanthrene	610	625,1625	610	
Phenol	604	625,1625	--	
Pyrene	610	625,1625	610	
2,3,7-8-Tetrachlorodibenzo-p-dioxane	--	613	--	
1,1,2,2-Tetrachloroethane	601	624,1624	--	p 130
Tetrachloroethene	601	624,1624	--	p 130
Toluene	602	624,1624	--	
1,2,4-Trichlorobenzene	601	624,1624	--	p 130
1,1,1-Trichloroethane	601	624,1624	--	
1,1,2-Trichloroethane	601	624,1624	--	p 130
Trichloroethene	601	624,1624	--	
Trichlorofluoromethane	601	624	--	
2,4-6-Trichlorophenol	604	625,1625	--	
Vinyl chloride	601	624,1624	--	

Table 2

Approved Test Procedures for Pesticides

Parameter	Method	EPA*	Standard Methods	ASTM	Other**
Aldrin	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
Ametryn	GC				a, p 83; c, p S68
Aminocarb	TLC				a, p 94; c, p S16
Atraton	GC				a, p 83; c, p S68
Atrazine	GC				a, p 83; c, p S68
Azinphos methyl	GC				a, p 25; c, p S51
Barban	TLC				a, p 104; c, p S64
Alpha BHC	GC	608	509A	D3086	a, p 7
	GC/MS	625			
Beta BHC	GC	608		D3086	
	GC/MS	625			
Delta BHC	GC	608		D3086	
	GC/MS	625			
gamma BHC (Lindane)	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
Captan	GC		509A		a, p 7
Carbaryl	TLC				a, p 94; c, p S60
Carbophenothion	GC				b, p 30; c, p S73
Chlordane	GC	608	509A	D3086	a, p 7
	GC/MS	625			
Chloroprophan	TLC				a, p 104; c, p S64
2,4-D	GC		509B		a, p 115; b, p 35
4,4'-DDD	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
4,4'-DDE	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
4,4'-DDT	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
Demeton-o	GC				a, p 25; c, p S51

(Continued)

Source: Federal Register (1984).

* The full texts of methods 608 and 625 are given in 40 CFR, Appendix A, Part 136, "Test Procedures for Analysis of Organic Pollutants."

** a. USEPA, 1978 (Sep), "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater."

b. USGS, 1972, "Methods for Analysis of Organic Substances in Water," Techniques of Water-Resources Investigation, Book 5, Chapter A3.

c. ASTM, 1981, "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater.

(Sheet 1 of 3)

Table 2 (Continued)

Parameter	Method	EPA	Standard Methods	ASTM	Other
Demeton-s	GC				a, p 25; c, p S51
Diazinon	GC				a, p 25; b, p 30; c, p S51
Dicamba	GC				a, p 115
Dichlofenthion	GC				b, p 30; c, p S73
Dichloran	GC		509A		a, p 7
Dicofol	GC			D3086	
Dieldrin	GC	608	509A		a, p 7; b, p 30
	GC/MS	625			
Dioxathion	GC				b, p 30; c, p S73
Disulfoton	GC				a, p ; c, p S51
Diuron	TLC				a, p 104; c, p S64
Endosulfan I	GC	608	509A	D3086	a, p 7
	GC/MS	625			
Endosulfan II	GC	608	509A	D3086	a, p 7
	GC/MS	625			
Endosulfan sulfate	GC	608			
	GC/MS	625			
Endrin	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
Endrin aldehyde	GC	608			
	GC/MS	625			
Ethion	GC				b, p 30; c, p S73
Fenuron	TLC				a, p 104; c, p S64
Fenuron-TCA	TLC				a, p 104; c, p S64
Heptachlor	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
Heptachlor epoxide	GC	608	509A	D3086	a, p 7; b, p 30; c, p S73
Isodrin	GC				b, p 30; c, p. S64
Linuron	TLC				a, p 104; c, p S64
Malathion	GC		509A		a, p 25; b, p 30; c, p S51
Methiocarb	TLC				a, p 94; c, p S60
Methoxychlor	GC		509A	D3086	a, p 7; c, p 30
Mexacarbate	TLC				a, p 94; c, p S60
Mirex	GC		509A		a, p 7
Monuron	TLC				a, p 104; c, p S64
Monuron-TCA	TLC				a, p 104; c, p S64
Neburon	TLC				a, p 104; c, p S64
Parathion methyl	GC		509A		a, p 25; b, p 30
Parathion ethyl	GC		509A		a, p 25
PCNB	GC		509A		a, p 7
Perthane	GC			D3086	
Prometon	GC				a, p 83; c, p S68

(Continued)

Table 2 (Concluded)

Parameter	Method	EPA	Standard Methods	ASTM	Other
Prometryn	GC				a, p 83; c, p S68
Propazine	GC				a, p 83; c, p S68
Propham	TLC				a, p 104; c, p S64
Propoxur	TLC				a, p 94; c, p S60
Secbumeton	TLC				a, p 83; c, p S68
Siduron	TLC				a, p 104; c, p S64
Simazine	GC				a, p 83; c, p S68
Strobane	GC		509A		a, p 7
Swep	GC				a, p 104; c, p S64
2,4,5-T	GC		509B		a, p 115; b, p 35
2,4,5-TP (Silvex)	GC		509B		a, p 115
Terbuthylazine	GC				a, p 83; c, p S68
Toxaphene	GC	608	509A	D3086	a, p 7; b, p 30
	GC/MS	625			
Trifluralin	GC		509A		a, p 7

Table 3

Quality Control Requirements and Frequency of Application

QC Parameter	Frequency	Comments
Matrix spikes	One per analytical batch per matrix or every 20 samples, whichever is greater.	
Replicates	One per analytical batch per matrix or every 20 samples, whichever is greater.	Replicate samples are separate aliquots taken from the same sample container in the laboratory and analyzed independently. Evaluation of replicate data can indicate the existing of gross errors in the analysis. In cases where aliquoting is impossible (i.e., volatiles), duplicate samples must be taken for replicate analysis.
Blanks	One per analytical batch per matrix or every 20 samples, whichever is greater.	
Field duplicates	One per analytical batch per matrix or every 20 samples, whichever is greater.	Field duplicate samples are two separate samples taken from the same sampling point in the field (i.e., in separate containers and analyzed independently). Evaluation of duplicate data can indicate the existence of gross errors in the sampling technique.
Check standard	One per analytical batch or every 20 samples, whichever is greater	
Surrogates	Add prescribed surrogates to every blank, standard, sample and QA sample.	Only for volatile and semivolatile organics and pesticides.
Column check sample	One per batch of adsorbent.	Applies to adsorbent chromatography and back extractions of organic compounds.
Column check sample blank	One per batch of adsorbent.	Applies to adsorbent chromatography and back extractions of organic compounds.

(Continued)

Table 3 (Concluded)

QC Parameter	Frequency	Comments
Standard curves	Refer to specific method for necessary periodic calibration.	As prescribed by specific methods.
GC/MS instrument performance check	Initial 5-point calibration is to be verified with a single-point calibration once every 12 hr of instrument operation and if the sensitivity and linearity criteria are not met, a new 5-point initial calibration must be generated.	Performed to meet tuning criteria of the instrument as specified in the GC/MS methods. Organic analytes shall be checked with a 4-bromofluorobenzene (BFB) for determination of volatiles and with decafluorotriphenyl phosphine (DFTPP) for determination of semivolatiles.

Table 4

Analysis Methods for Organic Chemicals Contained in SW-846

Compound	Method(s)
Acetonitrite	8030, 8240
Acetophenone	8250, 8270
Acrolein	8030, 8240
Acrylamide	8015
Acrylonitrile	8030, 8240
Aldrin	8080, 8250, 8270
4-Aminobiphenyl	8250, 8270
Aniline	8250, 8270
Benzal chloride	8120
Benzene	8020, 8021, 8240, 8260
Benzidine	8250, 8270
Benzo(b)fluoranthene	8100, 8250, 8270, 8310
Benzo(a)anthracene	8100, 8250, 8270, 8310
Benzo(j)fluoranthene	8100
Benzo(a)pyrene	8100, 8250, 8270, 8310
Benzotrichloride	8120
Benzyl chloride	8010, 8120, 8240
Bis(2-chloroethoxy)methane	8010, 8110, 8250, 8270
Bis(2-chloroethyl)ether	8110, 8250, 8270
Bis(2-chloroisopropyl)ether	8010, 8110, 8250, 8270
Bis(2-ethylhexyl)phthalate	8060, 8250, 8270
Bromoform	8010, 8021, 8240, 8260
4-Bromophenyl phenyl ether	8110, 8250, 8270
Butyl benzyl phthalate	8250, 8270
Carbon disulfide	8240
Carbon tetrachloride	8010, 8021, 8240, 8260
Chlordane	8080, 8250, 8270
Chlorinated biphenyls	8080
Chlorinated dibenzo-p-dioxins	8280
Chlorinated dibenzofurans	8280
4-Chloroaniline	8250, 8270
Chlorobenzene	8010, 8020, 8021, 8240, 8260
2-Chloroethyl vinyl ether	8010, 8240
Chloroform	8010, 8021, 8240, 8260
Chloromethane	8010, 8021, 8240, 8260
Chloromethylmethyl ether	8010
2-Chloronaphthalene	8120, 8250, 8270
2-Chlorophenol	8040, 8250, 8270
Chrysene	8100, 8250, 8270, 8310
Creosote*	8100, 8250, 8270
Cresol(s)	8040
Croyslic acid(s)	8040, 8250, 8270
2,4-D	8150

(Continued)

* Analyze for phenanthrene and carbazole; if these are present in a ratio between 1.4:1 and 5:1, creosote should be considered present.

(Sheet 1 of 3)

Table 4 (Continued)

Compound	Method(s)
4,4'-DDD	8080, 8250, 8270
4,4'-DDE	8080, 8250, 8270
4,4'-DDT	8080, 8250, 8270
Dibenz(a,h)acridine	8100
Dibenz(a,i)acridine	8100, 8250, 8270
Dibenz(a,h)anthracene	8100, 8250, 8270, 8310
7H-Dibenzo(c,q)carbazole	8100
Dibenzo(a,o)pyrene	8100, 8270
Dibenzo(a,h)pyrene	8100
Dibenzo(a,i)pyrene	8100
Di-n-butylphthalate	8060, 8250, 8270
Dichlorobenzene(s)	8010, 8020, 8021, 8120, 8220 8250, 8260
3,3'-Dichlorobenzidine	8250, 8270
Dichlorodifluoromethane	8010, 8021, 8240, 8260
Dichloroethane(s)	8010, 8021, 8240, 8260
1,1-Dichloroethylene	8010
1,2-Dichloroethylene	8010, 8240
Dichloromethane	8010
2,4-Dichlorophenol	8040, 8250, 8270
2,6-Dichlorophenol	8040, 8250, 8270
1,2-Dichloropropane	8010, 8021, 8240, 8260
trans-1,3-Dichlorophropylene	8010
Dichloropropene(s)	8240
Dieldrin	8080, 8250, 8270
Diethyl phthalate	8060, 8250, 8270
4-Dimethylaminozaobenzene	8250, 8270
7,12-Dimethylbenz(a)anthracene	8250, 8270
alpha-alpha-Dimethylphenethylamine	8250, 8270
2,4-Dimethylphenol	8040, 8250, 8270
Dimethyl phthalate	8060, 8250, 8270
Dinitrobenzene(s)	8090, 8270
2,4-Dinitrophenol	8040, 8250, 8270
2,4-Dinitrotoluene	8090, 8250, 8270
2,6-Dinitrotoluene	8090, 8250, 8270
Dinoseb	8150, 8260
Di-n-octylphthalate	8060
Diphenylamine	8250, 8270
1,2-Diphenylhydrazine	8250, 8270
Disulfoton	8140, 8270
Endosulfan(I & II)	8080, 8250, 8270
Endrin	8080, 8250, 8270
Ethyl ether	8015
Endrin metabolites	8080, 8250, 8270
Ethyl methanesulfonate	8250, 8270
Fluoranthene	8100, 8250, 8270, 8310

(Continued)

Table 4 (Concluded)

Compound	Method(s)
Heptachlor	8080, 8250, 8270
Heptachlor epoxide	8080, 8250, 8270
Hexachlorobenzene	8120, 8250, 8270
Hexachlorobutadiene	8021, 8120, 8250, 8260, 8270
Hexachlorocyclopentadiene	8210, 8250, 8270
Hexachloroethane	8120, 8250, 8270
Indeno(1,2,3-cd)pyrene	8100, 8250, 8270, 8310
Lindane	8080
Maleic anhydride	8250, 8270
Methoxychlor	8080, 8250, 8270
3-Methylcholanthrene	8100, 8250, 8270
Methyl ethyl ketone	8015
Methyl isobutyl ketone	8015, 8240
Methylmethanesulfonate	8250, 8270
Naphthalene	8021, 8100, 8250, 8270, 8310
Naphthoquinone	8090, 8270
1-Naphthylamine	8250, 8270
2-Naphthylamine	8250, 8270
4-Nitroaniline	8250, 8270
Nitrobenzene	8090, 8250, 8270
4-Nitrophenol	8040, 8250, 8270
N-Nitrosodibutylamine	8250, 8270
N-Nitrosodimethylamine	8250, 8270
N-Nitrosopiperdine	8250, 8270
Paraldehyde (trimer of acetaldehyde)	8015
Parathion	8140, 8141, 8270
Pentachlorobenzene	8250, 8270
Pentachloronitrobenzene	8250, 8270
Pentachlorophenol	8040, 8250, 8270
Phenacetin	8250, 8270
Phenol	8040, 8250, 8270
Phorate	8140, 8141
Phthalic anhydride	8270
2 Picoline	8240, 8250, 8270
Pronamide	8250, 8270
Tetrachlorobenzene(s)	8120, 8250, 8270
Tetrachloroethane(s)	8010, 8021, 8240, 8260
Tetrachloroethane	8010, 8021, 8240, 8260
Tetrachlorophenol	8040, 8250, 8270
Toluene	8020, 8021, 8240, 8260
Toxaphene	8080, 8250, 8270
1,2,4-Trichlorobenzene	8021, 8120, 8250, 8260, 8270
Trichloroethane(s)	8010, 8021, 8240
Trichloroethane	8010, 8021, 8240
Trichlorofluoromethane	8010, 8021, 8240
Trichlorophenol(s)	8040, 8250, 8270
Trichloropropane	8010, 8021, 8240
Vinyl chloride	8010, 8021, 8240, 8260
Xylene(s)	8020, 8021, 8240, 8260

CWA. The primary difference is that the "500" series is designed to maximize detectability at low levels and has more stringent performance criteria.

Table 5

Analytical Methods for Volatile Organic Compounds Regulated by The SWDA (1986)

Organic Method	EPA Method No.
Volatile halogenated organic compounds in water by purge and trap GC	502.1
Volatile organic compounds in water by purge and trap GC with photo-ionization and electrolytic conductivity detectors in series	502.2
Volatile aromatic and unsaturated compounds in water by purge and trap GC	503.1
1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in water by microextraction and GC	504
Volatile organic compounds in water by purge and trap GC/MS	524.1
Volatile organic compounds in water by purge and trap capillary column GC/MS	524.2

18. The Federal Register (1988) gave final approval for USEPA methods for organic chemicals originally regulated by NPDWR, as given in Table 6. In addition, USEPA has also approved Method D-3086-79, "Organochlorine Pesticides in Water" from ASTM (1988) or Method 509-A from Standard Methods for the Examination of Water and Wastewater (APHA 1984) or "Gas Chromatographic Methods for Analysis of Organic Substances in Water" from USGS (1971).

Contract Laboratory Program

19. Testing requirements for laboratories participating in USEPA's Contract Laboratory Program (CLP) are contained in the "USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration" (USEPA 1988). Very detailed QA/QC procedures are presented in this document. Analytical methods are based on USEPA's "600" series. The CLP was designed by USEPA to provide routine chemical analysis services for Superfund hazardous-waste investigations.

Table 6

Methods for Other Organic Contaminants Regulated by the SWDA

Procedure	EPA Method No.
Determination of chlorinated pesticides in ground water by GC with an electron capture detector	508
Determination of nitrogen and phosphorous-containing pesticides in ground water by GC with a nitrogen-phosphorus detector	507
Determination of chlorinated herbicides in drinking water	515
Solid phase extraction for endrin, lindane, methoxychlor, and toxaphene	SPE-500

Corps Projects for Dredged and Fill Material

20. Corps Division laboratories or contract laboratories performing work for the Corps must frequently analyze samples to meet requirements for projects related to dredged and fill material. Analytical procedures to support these projects are often taken from "Procedures for Handling and Chemical Analysis of Sediment and Water Samples" (Plumb 1981). The guidance for collection of surface water and sediment samples and sample preparation (i.e., elutriate preparation) is particularly beneficial.

Summarized Procedures with QC Recommendations

21. Summaries of selected procedures from the preceding references are presented in Appendix A to provide a compilation of specific QC criteria for the various methods. These selections were made based on their relevance to Corps projects.

PART IV: DATA MANAGEMENT, REPORTING, AND EVALUATION

22. This section addresses general data management and reporting requirements needed to make an assessment of analytical data quality.

Data Management

23. Each analytical laboratory must maintain a records management system that includes documents pertinent to the analytical performance of the laboratory.

a. Instrument maintenance. Records of maintenance for each instrument should contain information relating to repairs such as date, nature of the problem, and corrective action. Preventive maintenance records should also be filed.

b. Calibration. Instrument calibration records should be maintained in either a computer system or a permanent log book. Standards preparations and usage should be entered in a permanent log. Information should include origin of the standard, person preparing calibration standards and dilutions, concentrations of solutions and date prepared.

c. Sample preparation. Permanent laboratory notebooks should be maintained with records of all sample preparations including date, sample aliquot, type of extraction or other process, surrogates, spikes, duplicates, and final sample volume. Any unusual reactions should be noted.

d. Instrumental analysis files. Sample raw data files from instrumental analyses should be maintained on hard disks, floppy disks, magnetic tape, or other semipermanent storage so that sample data may be reconstructed if necessary. Requirements for data storage may be 1 to 7 years depending on project requirements.

e. Data verification. Data verification should be part of standard operating procedures and should be an integral part of the laboratory's QC program.

f. Corrective actions. Provision should be made for corrective action to be taken when any check of the analytical process indicates a problem. The solution may be as simple as data reentry or as major as complete reanalysis of a sample set.

Data Reporting

24. Requirements for data reports vary widely. The USEPA has 36 pages of forms for reporting organic analysis data for the CLP. The CE (Missouri

Division) has condensed this package to 26 pages for reporting organic analysis data for Superfund and Defense Environmental Restoration Program (DERP) Projects. Many sponsors want only sample concentrations without any supporting documentation. Regardless of the details required for final data reporting, the laboratory performing the analysis should have all supporting QA data available for review if it is ever needed. Basically this includes calibration data, sample analysis data, surrogate spike recovery data, replicate sample analysis data, matrix spike recovery data, method blank data, and external QA sample data.

Analysis Evaluation

25. Some type of evaluation is usually made on the quality of the data reported. It may consist of a statistical evaluation based on precision and accuracy data calculated from replicate and spiked sample analyses. It may be a common sense evaluation of how reasonable the data seem based on knowledge of the sample origins. It may be a trend analysis based on previous data collected. Regardless of the approach, documentation of QA/QC procedures beginning with field collection data and ending with laboratory data reporting is necessary to assure the authenticity of the analytical process. Quality control at every step of the procedure is essential if the final product is to be a valid assessment of the media being analyzed.

PART V: RECOMMENDATIONS

26. Personnel performing organic chemical analyses or contracting for analyses for environmental projects should become familiar with regulatory requirements mandating the use of specific methods and QA/QC. By adhering to approved procedures and good QA/QC practices, problems related to the production of environmental data can be avoided, and the Corps can enhance its reputation for producing quality products.

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_____. 1988. "USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration," Washington, DC.

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APPENDIX A: METHOD SUMMARIES WITH RECOMMENDED QUALITY ASSURANCE/ QUALITY CONTROL CRITERIA

Method 624, Purgeable Organics by Gas Chromatograph/Mass Spectrometer

1. This method covers the determination of purgeable organics in municipal and industrial discharges by purge-and-trap (P&T) gas chromatograph/ mass spectrometer (GC/MS) and is approved for testing requirements of the Clean Water Act. In Table A1 the method detection limit (MDL) for each purgeable is listed. These MDLs should be obtainable depending on the nature and level of interferences present in the water sample.

Summary of method

2. Helium is bubbled through a 5-ml water sample contained in a specially designed purging vessel at room temperature. The volatile compounds are purged from the water sample into the vapor phase. The vapor is passed through a trap held at ambient temperature, and the volatiles are trapped. The trap is heated rapidly to desorb the volatiles onto a gas chromatographic column. The gas chromatographic column is temperature programmed to separate the compounds that are directed into a MS for detection.

Equipment and operating conditions

3. The following equipment and operating conditions apply:

a. The P&T system is set up in the following manner:

(1) Purge: 11.0 min with 40-ml/min helium flow.

(2) Desorb: 4.0 min at 180° C with 40ml/min helium flow.

(3) Trap bake: 7.0 min at 180° C.

b. Gas chromatograph (GC):

(1) Column: 6-ft long by 1/8-in. inside diameter (ID) glass or stainless steel column packed with 1-percent SP-1000 on Carbopack B (60 to 80 mesh). Helium carrier gas is set at 30 ml/min.

(2) Temperature: Initially at 45° C for 3 min and then programmed at 8° C/min to 220° C and held for 15 min.

c. Mass spectrometer (MS): Scan from 20 to 260 amu every 7 sec or less to achieve at least 5 scans/peak with 70-V electron energy in the electron-impact ionization mode. The mass spectrum obtained must meet the criteria listed in Table A2 for 50-ng 4-bromofluorobenzene (BFB) injected through the GC inlet. The scanning of the MS should commence when the P&T begins the desorb mode.

Table A1

Method Detection Limits and Percent Recovery, Method 624

Compound Name	MDL µg/ℓ	Range for P, P_s,* %
Benzene	4.4	37-151
Bromodichloromethane	2.2	35-155
Bromoform	4.7	45-169
Bromomethane	nd**	D-242
Carbon tetrachloride	2.8	70-140
Chlorobenzene	6.0	37-160
Chloroethane	nd	14-230
2-Chloroethyl vinyl ether	nd	D-305
Chloroform	1.6	51-138
Chloromethane	nd	D-273
Dibromochloromethane	3.1	53-149
1,2-Dichlorobenzene	nd	18-190
1,3-Dichlorobenzene	nd	59-156
1,4-Dichlorobenzene	nd	18-190
1,1-Dichloroethane	4.7	59-155
1,2-Dichloroethane	2.8	49-155
1,1-Dichloroethene	2.8	D-234
trans-1,2-Dichloroethene	1.6	54-156
1,2-Dichloropropane	6.0	D-210
cis-1,3-Dichloropropene	5.0	D-227
trans-1,3-Dichloropropene	nd	17-183
Ethyl benzene	7.2	37-162
Methylene chloride	2.8	D-221
1,1,2,2-Tetrachloroethane	6.9	46-157
Tetrachloroethene	4.1	64-148
Toluene	6.0	47-150
1,1,1-Trichloroethane	3.8	52-162
1,1,2-Trichloroethane	5.0	52-150
Trichloroethene	1.9	71-157
Trichlorofluoromethane	nd	17-181
Vinyl chloride	nd	D-251

* P, P_s = percent recovery measured; D = detected, result must be greater than zero.

** nd = not determined.

Table A2

4-Bromofluorobenzene Key Mass/Charge (M/Z) Abundance Criteria, Method 624

Mass	M/Z Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% mass 174
177	5 to 9% of mass 176

d. Data system: The MS should be interfaced to a data system capable of recording and storing all mass spectra generated during the chromatographic run. The computer software must be capable of searching for specific M/Z values and integrating their abundance.

Interferences and contamination

4. All reagents, glassware, solvents, water, purge gas, etc., must be free of any compound(s) that would interfere with the volatiles analysis above the MDL for that parameter. In practice, this is hard to accomplish for such common solvents as methylene chloride and to some extent toluene and benzene. Carry-over between analyses can be particularly troublesome when high-level samples are followed by low-level ones.

Identification

5. To make a qualitative identification of a parameter, the following criteria must be met:

a. The primary and secondary M/Z values must maximize in the same or one full spectrum scan of each other.

b. The retention time (RT) of the unknown must fall within ±30 sec of the standard.

c. The relative peak height of the M/Z values selected must be within ±20 percent of these values in the standard.

Structural isomers of similar mass are very difficult to identify even with these criteria. Adequate chromatographic resolution must be accomplished to assure a good identification in this case.

Quality assurance
(QA)/quality control (QC)

6. A laboratory that performs Method 624 is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored.

b. The laboratory must spike and duplicate 5 percent of all samples on a continuing basis to evaluate data quality against the original control charts. These data should be added to the control charts periodically to update them. The spike value should be in the range of 1 to 5 times the value in the samples. As an analyst becomes more proficient at an analysis, the tighter the ranges on the control chart will become.

c. A reagent water blank should be analyzed each day to verify that the entire system is free of any analytical interfences for the parameters analyzed.

d. The analyst must verify at the beginning of each shift that the established calibration curve is still valid through the analysis of a 20-µg/ℓ check standard containing all parameters of interest. If any compounds fall outside the acceptance criteria of Table A3, the problem must be corrected and reanalysis performed.

e. Any parameter result beyond the calibrated range must be diluted within range.

f. The laboratory must spike each sample analyzed with at least three of the surrogates listed in Table A4 and monitor the percent recovery. This is best accomplished by adding the surrogates to the initial samples to check precision and accuracy. Calculate the average percent recovery (R) of the surrogates and their standard deviation (SD). The recovery of the surrogates in each sample must fall within $R \pm 3\ SD$, or the sample must be reanalyzed.

g. All calibrations should be calculated by the internal standard method. Suggested internal standards are listed in Table A4. The internal standard method best compensates for any instrument irregularities and aids in the identification by use of relative RTs.

h. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Table A3

Calibration and QC Acceptance Criteria,* Method 624

Compound Name	Range for Q** µg/ℓ	Limit for SD,† µg/ℓ	Range for X,†† µg/ℓ
Benzene	12.8-27.2	6.9	15.2-26.0
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0
Bromoform	14.2-25.8	5.4	11.4-31.1
Bromomethane	2.8-37.2	17.9	D-41.2
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5
Chlorobenzene	13.2-26.8	6.3	16.4-27.4
Chloroethane	7.6-32.4	11.4	8.4-40.4
2-Chloroethyl vinyl ether	D-44.8	25.9	D-50.4
Chloroform	13.5-26.5	6.1	13.7-24.2
Chloromethane	D-40.8	19.8	D-45.9
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.5
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.5
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4
Ethyl benzene	11.8-28.2	7.5	17.4-26.7
Methylene chloride	12.1-27.9	7.4	D-41.0
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6
Toluene	14.9-25.1	4.8	16.6-26.7
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1
Trichloroethene	13.3-26.7	6.6	18.6-27.6
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5
Vinyl chloride	0.8-39.2	20.0	D-43.5

* Criteria were calculated assuming a QA check sample concentration of 20 µg/ℓ.

** Q = concentration measured in QC check sample.

† SD = standard deviation of four recovery measurements.

†† X = average recovery of four recovery measurements; D = detected, result must be greater than zero.

Table A4

Suggested Surrogate and Internal Standards, Method 624

Compound	Retention Time, min	Primary M/Z	Secondary Masses
Benzene-d_6	17.0	84	--
4-Bromofluorobenzene	28.3	95	174, 176
1,2-Dichloroethane-d_4	12.1	102	--
1,4-Difluorobenzene	19.6	114	63, 88
Ethylbenzene-d_5	26.4	111	--
Ethylbenzene-d_{10}	26.4	98	--
Fluorobenzene	18.4	96	70
Pentaflorobenzene	23.5	168	--
Bromochloromethane	9.3	128	49, 130, 51
2-Bromo-1-chloropropane	19.2	77	79, 156
1,4-Dichlorobutane	25.8	55	90, 92

Method 8240, Purgeable Organics by GC/MS

7. Method 8240 covers the determination of the purgeable organics listed in Table A5 in a variety of solid and liquid matrices by purge-and-trap GC/MS. This method is applicable to the analysis of most purgeable organic compounds with boiling points below 200° C and varying solubilities in water. However, the practical quantitation limit (PQL) will vary depending on the purging efficiency of the compound. A prerequisite is that the analyte elutes as a sharp peak from the chromatographic column used. In Table A5 the PQL for each evaluated volatile organic compound is listed. These PQLs should be obtainable depending on the nature and level of interferences present in the sample.

Summary of method

8. Helium is bubbled through a water solution contained in a specially designed purging vessel at room temperature. The volatile compounds are purged from the sample into the vapor phase. The vapor is passed through a trap held at ambient temperature, and the volatiles are trapped. The trap is heated rapidly to desorb the volatiles onto the gas chromatographic column. The GC is temperature programmed to separate the compounds that are directed into the MS for detection. In some instances (medium- or high-level soils or sediments), it is more appropriate to extract the sample with methanol. When

Table A5

Practical Quantitation Limits (PQL)* and Percent Recovery,** Method 8240

Compound Name	PQL† Ground Water µg/ℓ	PQL† Low Soil/Sediment µg/kg	Range P, P_s,††%
Chloromethane	10	10	D-273
Bromomethane	10	10	D-242
Vinyl Chloride	10	10	D-251
Chloroethane	10	10	nd‡
Methylene chloride	5	5	D-221
Acetone	100	100	nd
Carbon disulfide	5	5	nd
1,1-Dichloroethene	5	5	D-234
1,1-Dichloroethane	5	5	59-155
trans-1,2-Dichloroethene	5	5	54-156
Chloroform	5	5	51-138
1,2-Dichloroethane	5	5	49-155
2-Butanone	100	100	nd
1,1,1-Trichloroethane	5	5	52-162
Carbon tetrachloride	5	5	70-140
Vinyl acetate	50	50	nd
Bromodichloromethane	5	5	35-155
1,1,2,2-Tetrachloroethane	5	5	46-157
1,2-Dichloropropane	5	5	D-210
trans-1,3-Dichloropropene	5	5	17-183
Trichloroethene	5	5	71-157
Dibromochloromethane	5	5	53-149
1,1,2-Trichloroethane	5	5	52-150
Benzene	5	5	37-151
cis-1,3-Dichloropropene	5	5	D-227
2-Chloroethyl vinyl ether	10	10	D-305
Bromoform	5	5	45-169
2-Hexanone	50	50	nd
4-Methyl-2-pentanone	50	50	nd
Tetrachloroethene	5	5	68-148
Toluene	5	5	47-150
Chlorobenzene	5	5	37-160
Ethyl benzene	5	5	37-162
Styrene	5	5	nd
Total xylenes	5	5	nd
1,2-Dichlorobenzene	nd	nd	18-190
1,3-Dichlorobenzene	nd	nd	59-156
1,4-Dichlorobenzene	nd	nd	18-190
Trichlorofluoromethane	nd	nd	17-181

* Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

** From 40 CFR Part 136 for Method 624, calculated using a 20-µg/ℓ check sample of each parameter.

† Based on wet weight.

†† P, P_s = percent recovery measured.

‡ nd = not determined.

this technique is used, a portion of the methanol extract is added to reagent water in the purge vessel and the previous steps are followed.

Equipment and operating conditions

9. The following equipment and operating conditions apply:

   a. The P&T system is set up in the following manner:

      (1) Purge: 11.0 min with 40-ml/min helium flow.

      (2) Desorb: 4.0 min at 180° C with 40-ml/min helium flow.

      (3) Trap bake: 7.0 min at 180° C.

   b. Gas chromatograph:

      (1) Column: 6 ft long by 1/8-in.-ID glass or stainless steel column packed with 1-percent SP-1000 on Carbopack B (60 to 80 mesh). Helium carrier gas is set at 30 ml/min.

      (2) Temperature: Initially at 45° C for 3 min and then programmed at 8° C/min to 220° C and held for 15 min.

   c. Mass spectrometer: Scan from 35 to 250 amu every 7 sec or less to achieve at least 5 scans/peak with 70-V electron energy in the electron impact ionization mode. The mass spectrum obtained must meet the criteria listed in Table A6 for 50-ng BFB injected through the GC inlet. The scanning of the MS should commence when the P&T begins the desorb mode.

   d. Data system: The MS should be interfaced to a data system capable of recording and storing all mass spectra generated during the chromatographic run. The computer software must be capable of searching specific M/Z values and integrating their abundance. The most recent version of the US Environmental Protection Agency/National Institutes of Health (EPA/NIH) Mass Spectral Library should be available to facilitate the identification of any unknown compounds in the gas chromatographic run if requested.

Table A6

4-Bromofluorobenzene Key Ion Abundance Criteria, Method 8240

Mass	M/Z Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% mass 174
177	5 to 9% of mass 176

Interferences and contamination

10. All reagents, glassware, solvents, reagent water, purge gas, etc., must be free of any compound(s) that would interfere with the purgeables analysis above the PQL for that parameter. In practice, this is hard to accomplish for such common solvents as methylene chloride, acetone, and to some extent benzene and toluene.

11. Because of the nature and type of samples analyzed by this method, interferences purged or coextracted by methanol will vary from each sample source and can greatly influence the analytical result.

12. Carry-over between analyses can be particularly troublesome when high-level samples are followed by low-level ones.

Identification

13. Qualitative. To make a qualitative identification of a parameter, the following criteria must be met:

a. The primary and secondary M/Z values must maximize in the same or one full spectrum scan of each other.

b. The unknown relative retention time (RRT) must agree within ±0.06 RRT units of the RRT of the compound in the standard run.

c. The relative peak intensities of the specified M/Z values must be within ±20 percent of those values in the standard.

d. All ions present in the standard mass spectra above 10-percent relative intensity to the base peak must be present in the sample component.

14. An EPA/NIH library search may be requested of any unknown components present in the sample. Guidelines for the evaluation of a tentative identification of the unknown sample component are:

a. Relative intensities of the major M/Z values in the library spectrum above 10 percent relative to the base peak should be present.

b. Relative intensities of these major ions should agree within ±20 percent.

c. Molecular ions present in the library spectrum should be in the sample component.

15. After the computer search, the mass spectral interpretation specialist should evaluate the resultant tentative identification.

16. Quantitative. To make a quantitative identification of a parameter, the following criteria must be met:

a. Identified compounds. Quantification of the identified sample compound must be by the internal standard technique. The

recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. The internal standards along with their corresponding analytes are listed in Table A7. Liquid samples are normally reported in micrograms per litre. Sediment samples are usually reported in micrograms per kilogram on a dry weight basis, while sludges and waste are reported on a wet weight basis.

Table A7

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation, Method 8240

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Acetone	Benzene	Bromofluorobenzene (surrogate)
Acrolein	Bromodichloromethane	Chlorobenzene
Acrylonitrile	Bromoform	Ehtylbenzene
Bromomethane	2-Butanone	Ethyl methacrylate
Carbon disulfide	Carbon tetrachloride	2-Hexanone
Chloroethane	Chlorodibromomethane	4-Methyl-2-pentanone
Chloroform	2-Chloroethyl vinyl ether	Styrene
Chloromethane	Dibromomethane	1,1,2,2-Tetrachloroethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene	1,1,2,2-Tetrachloroethane
1,1-Dichloroethane	1,2-Dichloropropane	Toluene
1,2-Dichloroethane	cis-1,3-Dichloropropane	Toluene-d_8 (surrogate)
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene	1,2,3-Trichloropropane
1,1-Dichloroethene	1,1,1-Trichloroethane	Xylene
trans-1,2-Dichloroethene	1,1,2-Trichloroethane	
Iodomethane	Trichloroethene	
Methylene chloride	Vinyl acetate	
Trichlorofluoromethane		
Vinyl Chloride		

b. Tentatively identified compounds. Tentatively identified sample components can be estimated by the internal standard approach using the nearest RT internal standard that is free of interferences. The response factor (RF) is assumed to be 1.

Quality assurance/quality control

17. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. Acceptable precision and accuracy are listed in Table A8.

Table A8

Calibration and QC Acceptance Criteria,* Method 8240

Compound Name	Range for Q,** µg/ℓ	Limit for SD,† µg/ℓ	Range for X,†† µg/ℓ
Benzene	12.8-27.2	6.9	15.2-26.0
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0
Bromoform	14.2-25.8	5.4	11.4-31.1
Bromomethane	2.8-37.2	17.9	D-41.2
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5
Chlorobenzene	13.2-26.8	6.3	16.4-27.4
2-Chloroethyl vinyl ether	D-44.8	25.9	D-50.4
Chloroform	13.5-26.5	6.1	13.7-24.2
Chloromethane	D-40.8	19.8	D-45.9
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0
trans-1,3-Dochloropropene	10.0-30.0	10.4	7.6-32.4
Ethyl benzene	11.8-28.2	7.5	17.4-26.7
Methylene chloride	12.1-27.9	7.4	D-41.0
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6
Toluene	14.9-25.1	4.8	16.6-26.7
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1
Trichloroethene	13.3-26.7	6.6	18.5-27.6
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5
Vinyl chloride	0.8-39.2	20.0	D-43.5

* Criteria from 40 CFR Part 136 for Method 624, calculated assuming a QC check sample concentration of 20 µg/ℓ.

** Q = concentration measured in QC check sample.

† SD = standard deviation of four recovery measurements.

†† X = average recovery for four recovery measurements; D = detected, result must be greater than zero.

b. The laboratory must perform a matrix spike and matrix spike duplicate on 5 percent of all samples on a continuing basis to evaluate data quality against the original control charts. These data should be added to the control charts periodically to update them. The spike value should be in the range of 1 to 5 times the value in the samples. As an analyst becomes more proficient at an analysis, the tighter the ranges on the control chart will become.

c. A reagent water blank should be analyzed each day to verify that the system is free of any analytical interferences for the parameters analyzed.

d. The analyst must verify at the beginning of each shift that the analytical system is operating properly through the analysis of a set of compounds named System Performance Check Compounds (SPCCs). They are chloromethane, bromoform, 1,1,2,2-tetrachloroethane, 1,1-dichloroethane, and chlorobenzene. The SPCCs are checked for an average minimum response factor (RF) of 0.300 (0.250 for bromoform). Lower RFs for these compounds will typically result from too high or low purge gas flow and/or contaminated or active sites in the purge and trap system, GC inlet, GC column, GC transfer line to MS, and the jet separator.

e. After the SPCCs are checked, the analyst must verify that the established 5-point calibration curve is still valid through the analysis of a set of compounds called Calibration Check compounds (CCCs). The CCCs are 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride. The percent difference for each CCC cannot exceed 25 percent with 20 percent used as a warning limit. Some of the same problems that affected the SPCCS are valid here. The retention time of the internal standards should not change by more than 30 sec from any previous CCC checks. When this occurs, there is likely to be a chromatographic problem. During the initial method validation (item a), the CCCs relative standard deviation should be less than 30 percent.

f. Any parameter result that is beyond the calibrated range must be diluted within range.

g. The laboratory must spike each sample analyzed with the three surrogate compounds listed in Table A9. After a minimum of 30 samples of the sample matrix are analyzed, a control chart based on percent R of each surrogate and their standard deviation must be prepared. The R for each surrogate should fall within ±3 SD, or the sample must be reanalyzed. Each ±3-SD surrogate range should fall within the guidelines of Table A9.

Table A9

Surrogate Spike Recovery Limits for Water and Soil Sediment Samples, Method 8240

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1-2 Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

h. The laboratory should on a continuing basis analyze external QC blind samples to check method performance.

Method 8010, Halogenated Volatile Organics by Gas Chromatography

18. Method 8010 is applicable to the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and covers the determination of the purgeable organics listed in Table A10 in a variety of solid and liquid matrices by gas chromatography with a halogen-specific detector. The injection technique used is either by purge and trap or direct injection. Direct injection has very limited applications because of the approximately 10,000 ug/ℓ detection limits. Also, Table A10 lists the MDL for halogenated volatile organics in reagent water. The PQL for the compounds in other matrices is listed in Table A11. The PQLs should be obtainable depending on the nature and level of interferences present in the sample.

19. This method is applicable to the analysis of most purgeable halogenated organic compounds with boiling points below 200° C and varying solubilities in water. However, the PQL will vary depending on the purging efficiency of the compounds. A prerequisite is that the analyte elutes as a sharp peak from the chromatographic column used.

Summary of method

20. Helium is bubbled through a water solution contained in a specially designed purging vessel at room temperature. The volatile compounds are purged from the sample into the vapor phase. The vapor is passed through a trap held at ambient temperature, and the volatiles are trapped. The trap is heated rapidly to desorb the volatiles onto the gas chromatographic column. The GC is temperature programmed to separate the compounds which are detected by a halogen specific detector. In some instances (medium- or high-level soils or sediments), it is more appropriate to extract the sample with methanol. When this technique is used, a portion of the methanol extract is added to reagent water in the purge vessel and the previous steps followed.

Equipment and operating conditions

21. The following equipment and operating conditions apply:

a. The P&T system is set up in the following manner:

Table A10

Method Detection Limits for Halogenated Volatile Organics, Method 8010

Compound	MDL,* µg/ℓ
Benzyl chloride	
Bis(2-chloroethoxy)methane	
Bis(2-chloroisopropyl) ether	
Bromobenzene	
Bromodichloromethane	0.10
Bromoform	0.20
Bromomethane	
Carbon tetrachloride	0.12
Chloroacetaldehyde	
Chlorobenzene	0.25
Chloroethane	0.52
Chloroform	0.05
1-Chlorohexane	
2-Chloroethyl vinyl ether	0.13
Chloromethane	0.08
Chloromethyl methyl ether	
Chlorotoluene	
Dibromochloromethane	0.09
Dibromomethane	
1,2-Dichlorobenzene	0.15
1,3-Dichlorobenzene	0.32
1,4-Dichlorobenzene	0.24
Dichlorodifluoromethane	
1,1-Dichloroethane	0.07
1,2-Dichloroethane	0.03
1,1-Dichloroethylene	0.13
trans-1,2-Dichloroethylene	0.10
Dichloromethane	
1,2-Dichloropropane	0.04
trans-1,3-Dichloropropylene	0.34
1,1,2,2-Tetrachloroethane	0.03
1,1,1,2-Tetrachloroethane	
Tetrachloroethylene	0.03
1,1,1-Trichloroethane	0.03
1,1,2-Trichloroethane	0.02
Trichloroethylene	0.12
Trichlorofluoromethane	
Trichloropropane	
Vinyl chloride	0.18

* Using P&T method (Method 5030).

Table A11

Determination of PQL for Various Matrices,* Method 8010

Matrix	Factor**
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1250
Nonwater miscible waste	1250

* Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

** PQL = [MDL (Table A10)] × [Factor (Table A11)]. For nonaqueous samples, the factor is on a wet-weight basis.

(1) Purge: 11.0 min with 40-ml/min helium or nitrogen flow with trap at ambient temperature.

(2) Desorb: 4.0 min at 180° C with 40-ml/min helium or nitrogen flow.

(3) Trap bake: 7.0 min at 180° C.

b. Gas chromatograph:

(1) Column 1: 8-ft by 0.1-in.-ID glass or stainless steel column packed with 1-percent SP-1000 on Carbopack-B 60/80 mesh and a helium carrier gas flow of 40 ml/min. The column is temperature programmed as follows: 45° C for 3 min; then 8° C/min until a final temperature of 220° C is reached and held for 15 min.

(2) Column 2: 6-ft by 0.1-in.-ID glass or stainless steel column packed with chemically bonded n-octane on Porasil-C 100/200 mesh and a helium carrier gas flow of 40 ml/min. The column is temperature programmed as follows: 50° C for 3 min; then 6° C/min until a final temperature of 170° C is reached and held for 4 min.

(3) Detector: Electrolytic conductivity.

c. Data systems: A data system is preferred for the measurement of peak areas or heights and RTs from the point of desorption.

Interferences and contamination

22. All reagents, glassware, solvents, reagent water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the halogenated volatile organics analysis (VDA) above the MDL for that parameter. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between

analyses can be troublesome when high-level samples are followed by low-level ones. The purging system should be rinsed with reagent water and a reagent blank run to reduce and check for this occurrence. A field or trip blank should be prepared to check for any possibility of the samples becoming contaminated by diffusion of volatile organics (particularly Freon compounds) through the sample container septum.

Identification and quantification

23. Identification and quantification are usually accomplished by the external standard procedure. By this approach, the analyst matches the RT of the peak(s) present in the standards with peaks in the sample. Identifications based on RT should take into account any RT changes occurring during the analysis of standards analyzed before and after the samples. For example, 2 SD are used as a warning limit, and 3 SD are used as an outmost limit in tne calculation of RT windows for identification.

24. Quantitation is based on area or height response of the detected parameter versus concentration derived from a 5-point calibration curve. When the external standard approach is used, it is particularly important to confirm all positive identifications on a GC column of differing polarity from the main analytical column. This will add more creditability to the identification.

Quality assurance/quality control

25. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. The resultant precision and accuracy data must fall within the guidelines of Table A12.

b. The laboratory must analyze a reagent blank, matrix spike, and matrix spike duplicate/duplicate as a minimum for each analytical batch up to 20 samples. The spike value should be in the range of 1 to 5 times the value in the samples. After the analysis of five spiked samples (same matrix type), the accuracy can be expressed in control charts as average recovery ±2 SD to monitor data quality.

c. The laboratory must routinely analyze a check standard sample containing all parameters of interest. The need for check standard sample analysis increases with the complexity of the

sample matrix and the number of analytes present. If an analyte spike value falls outside the range of recoveries (from the QC chart, item b) a check standard sample must be analyzed. The concentration for the check sample concentrate using all parameters of interest is 20 µg/ℓ. The QC guidelines in Table A12 must be met.

Table A12

Calibration and QA Acceptance Criteria,* Method 8010

Parameter	Range for Q ** µg/ℓ	Limit for SD† µg/ℓ	Range for X†† µg/ℓ	Range P, P_s ‡ %
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.6	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.6	11.8-25.3	43-143
Chlorobenzene	14.4-25.6	5.0	10.2-27.4	38-150
Chloroethane	15.4-24.6	4.4	11.3-25.2	46-137
2-Chloroethyl vinyl ether	12.0-28.0	8.3	4.5-35.5	14-186
Chloroform	15.0-25.0	4.5	12.4-24.0	49-133
Chloromethane	11.9-28.1	7.4	D-34.9	D-193
Dibromochloromethane	13.1-26.9	6.3	7.9-35.1	24-191
1,2-Dichlorobenzene	14.0-26.0	5.5	1.7-38.9	D-208
1,3-Dichlorobenzene	9.9-30.1	9.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.6	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
Methylene chloride	15.5-24.5	4.0	7.0-27.6	25-162
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	5.7	8.2-29.9	28-163

* Criteria from 40 CFR Part 136 for Method 601, calculated assuming a QC check sample concentration of 20 µg/ℓ.

** Q = concentration measured in QC check sample.

† SD = standard deviation of four recovery measurements.

†† X = average recovery of four recovery measurements.

‡ P, P_s = percent recovery measured; D = detected, result must be greater than zero.

d. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

e. The analyst must verify at the beginning of each shift that the established 5-point calibration curve is valid by the analysis of one or more calibration standards. The response should be with 15 percent of the original response.

f. A mid-level calibration standard should be run after each group of 10 samples to verify the initial calibration.

g. The surrogates recommended for use in this analysis are a combination of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Each sample, blank, and spike must contain the surrogates. Once a minimum of 30 samples of the same matrix type have been analyzed, the average percent R and standard deviation of the percent recovery for each surrogate can be calculated. The method performance for the surrogates should be calculated as $R \pm 3\ SD$.

h. Any parameter result that is beyond the calibrated range must be diluted within range.

i. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Method 8020, Aromatic Volatile Organics

26. Method 8020 covers the determination of the purgeable aromatic organic compounds listed in Table A13 in a variety of solid and liquid matrices by GC with photo-ionization detection. The injection technique used is either by P&T or by direct injection. Direct injection has very limited applications because of the approximately 10,000 µg/ℓ detection limits. Table A13 also lists the MDL for the purgeable aromatic compounds in reagent water. The PQL for the aromatic compounds in other matrices is listed in Table A14. The PQLs should be obtainable depending on the nature and level of interferences present in sample.

27. This method is applicable to the analysis of most purgeable aromatic organic compounds with boiling points below 200° C and varying solubilities in water. However, the PQL will vary depending on the purging efficiency of the compounds. A prerequisite is that the analyte elutes as a sharp peak from the chromatographic column used.

Summary of method

28. Helium is bubbled through a water solution contained in a specially designed purging vessel at room temperature. The volatile compounds are

Table A13

Method Detection Limits for Aromatic Volatile Organics, Method 8020

Compound	MDL,* µg/ℓ
Benzene	0.2
Chlorobenzene	0.2
1,4-Dichlorobenzene	0.3
1,3-Dichlorobenzene	0.4
1,2-Dichlorobenzene	0.4
Ethyl benzene	0.2
Toluene	0.2
Xylenes	--

* Using P&T method (Method 5030).

Table A14

Determination of PQL for Various Matrices,* Method 8020

Matrix	Factor**
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1,250
Nonwater miscible waste	1,250

* Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

** PQL= [MDL (Table A13)] × Factor [(Table A14)]. For nonaqueous samples, the factor is on a wet-weight basis.

purged from the sample into the vapor phase. The vapor is passed through a trap held at ambient temperature, and the volatiles are trapped. The trap is heated rapidly to desorb the volatiles onto the gas chromatographic column. The GS is temperature programmed to separate the compounds detected by a photoionization detector. In some instances (medium- or high-level soils or sediments), it is more appropriate to extract the sample with methanol. When this technique is used, a portion of the methanol extract is added to reagent water in the purge vessel, and these same steps are followed.

Equipment and operating conditions

29. The following equipment and operating conditions apply:

a. The P&T system is set up as follows:

(1) Purge: 11.0 min with 40-ml/min helium or nitrogen flow with trap at ambient temperature.

(2) Desorb: 4.0 min at 180° C with 40 ml/min helium or nitrogen flow.

(3) Trap bake: 7.0 min at 180° C.

b. Gas chromatograph:

(1) Primary Column: 6-ft by 0.082-in.-ID #304 stainless steel or glass column packed with 5-percent SP-1200 and 1.75-percent Bentone-34 on 100/120 mesh Supelcoport and a helium carrier gas flow of 36 ml/min. For lower boiling compounds, the column is held at 50° C for 2 min and programmed 6° C/min to 90° C and held until all compounds of interest have eluted. This column has the unique ability of being able to resolve the three xylene isomers.

(2) Secondary column: 8-ft by 0.1-in.-ID stainless steel or glass column packed with 5-percent 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW and a helium carrier gas flow of 30 ml/min. The column is temperature programmed as follows: 40° C for 2 min; then 2° C/min until 100° C and held until all compounds have eluted. This column has been used to resolve aromatic hydrocarbons from alkanes in complex matrices.

(3) Detector: Photoionization (PID).

c. Data system: A data system is preferred for the measurement of peak areas or heights and RTs from the point of desorption.

Interferences and contamination

30. All reagents, glassware, solvents, reagent water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the halogenated VOA above the MDL for that parameter. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be troublesome when high-level samples are followed by low-level ones. The purging system should be rinsed with reagent water and a reagent blank run to reduce and check for this occurrence. A field or trip blank should be prepared to check for any possibility of the samples becoming contaminated by diffusion of volatile organics (particularly Freon compounds) through the sample container septum.

Identification and quantification

31. Identification and quantification are usually accomplished by the external standard procedure. By this approach the analyst matches the RT of the peak(s) present in the standards with peaks in the sample. Identifications based on RT should take into account any RT changes occurring during the

analysis of standards analyzed before and after the samples. For example, 2 SD are used as a warning limit, and 3 SD are used as an outmost limit in the calculation of RT windows for identification.

32. Quantitation is based on area or height response of the detected parameter versus concentration derived from a 5-point calibration curve. When the external standard approach is used, it is particularly important to confirm all positive identifications on a GC column of differing polarity from the main analytical column. This will add more creditability to the identification.

Quality assurance/quality control

33. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. The resultant precision and accuracy data must fall within the guidelines of Table A15.

Table A15

Calibration and QA Acceptance Criteria,* Method 8020

Parameter	Range for Q** µg/ℓ	Limit for SD† µg/ℓ	Range for X †† µg/ℓ	Range P, P_s ‡ %
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

* Criteria from 40 CFR Part 136 for Method 602, calculated assuming a QC check sample concentration of 20 µg/ℓ.
** Q = concentration measured in QC check sample.
† SD = standard deviation of four recovery measurements.
†† X = average recovery of four recovery measurements.
‡ P, P_s = percent recovery measured.

b. The laboratory must analyze a reagent blank, matrix spike, and matrix spike duplicate/duplicate as a minimum for each analytical batch up to 20 samples. The spike value should be in the range of 1 to 5 times the value in the samples. After the analysis of five spiked samples (same matrix type), the accuracy can be expressed in control charts as average recovery ±2 SD to monitor data quality.

c. The laboratory must routinely analyze a check standard sample containing all parameters of interest. The need for check sample analysis increases with the complexity of the sample matrix and the number of analytes present. If an analyte spike value falls outside the range of recoveries (from the QC chart, item b) a check standard sample must be analyzed. The concentration for the check sample concentrate using all parameters of interest is 20 µg/ℓ. The QC guidelines in Table A15 must be met.

d. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

e. The analyst must verify at the beginning of each shift that the established 5-point calibration curve is valid by the analysis of one or more calibration standards. The response should be within 15 percent of the original response.

f. A mid-level calibration standard should be run after each group of 10 samples to verify the initial calibration.

g. The surrogate recommended for use in this analysis is alpha, alpha, alpha-trifluorotoluene.

h. Any parameter result beyond the calibrated range must be diluted within range.

i. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Method 625, Base Neutral and Acid Extractable Compounds by GC/MS

34. Method 625 covers the analysis of the following base neutral and acid extractable organic compounds (Table A16) by GC/MS. In Table A16 the method detection limit (MDL) for each extractable organic is listed. These MDLs should be obtainable depending on the nature and level of interferences present in the water sample. Alpha-BHC, gamma-BHC, endosulfan I and II, and endrin are subject to decomposition due to the basic extraction conditions and are best analyzed by Method 608. Hexachlorocyclopentadiene is subject to thermal decomposition in the injection port of the GC and is preferably analyzed by Method 612. N-nitrosodiphenylamine decomposes in the injection port

Table A16

Method Detection Limits and Percent Recovery, Method 625

Compound Name	Method Detection Limit, µg/ℓ	Range for P, P_s,* %
1,3-Dichlorobenzene	1.9	D-172
1,4-Dichlorobenzene	4.4	20-124
Hexachloroethane	1.6	40-113
Bis(2-chloroethyl) ether	5.7	12-158
1,2-Dichlorobenzene	1.9	32-129
Bis(2-chloroisopropyl) ether	5.7	36-166
N-Nitrosodi-n-propylamine	--	D-230
Nitrobenzene	1.9	35-180
Hexachlorobutadiene	0.9	24-116
1,2,4-Trichlorobenzene	1.9	44-142
Isophorone	2.2	21-196
Naphthalene	1.6	21-133
Bis(2-chloroethoxy)methane	5.3	33-184
Hexachlorocyclopentadiene	--	--
2-Chloronaphthalene	1.9	60-118
Acenaphthylene	3.5	33-145
Acenaphthene	1.9	47-145
Dimethyl phthalate	1.6	D-112
2,6-Dinitrotoluene	1.9	50-158
Fluorene	1.9	59-121
4-Chlorophenyl phenyl ether	4.2	25-158
2,4-Dinitrotoluene	5.7	39-139
Diethyl phthalate	1.9	D-114
N-Nitrosodiphenylamine	1.9	nd
Hexachlorobenzene	1.9	D-152
Alpha-BHC	--	nd
4-Bromophenyl phenyl ether	1.9	53-127
Beta-BHC	--	24-149
Phenanthrene	5.4	54-120
Anthracene	1.9	27-133
Gamma-BHC	4.2	nd
Heptachlor	1.9	D-192
Delta-BHC	3.1	0-110
Aldrin	1.9	D-166
Di-n-butyl phthalate	2.5	1-118
Heptachlor epoxide	2.2	26-155
Endosulfan I	--	nd
Fluoranthene	2.2	26-137
Dieldrin	2.5	29-136
4,4'-DDE	5.6	4-136

(Continued)

* P, P_s = percent recovery measured; D = detected, result must be greater than zero; nd = not determined.

Table A16 (Concluded)

Compound Name	Method Detection Limit, µg/ℓ	Range for P, P_s,%
Pyrene	1.9	52-115
Endrin	--	nd
Endosulfan II	--	nd
4,4'-DDD	2.8	D-145
Benzidine	44	nd
4,4'-DDT	4.7	D-203
Endosulfan sulfate	5.6	D-107
Endrin aldehyde	--	D-209
Butyl benzyl phthalate	2.5	D-152
Bis(2-ethylhexyl) phthalate	2.5	8-158
Chrysene	2.5	17-168
Benzo(a)anthracene	7.8	33-143
3,3'-Dichlorobenzidine	16.5	D-262
Di-n-octyl phthalate	2.5	4-146
Benzo(b)fluoranthene	4.8	24-159
Benzo(k)fluoranthene	2.5	11-162
Benzo(a)pyrene	2.5	17-163
Indeno(1,2,3-c,d)pyrene	3.7	D-171
Dibenzo(a,h)anthracene	2.5	D-227
Benzo(g,h,i)perylene	4.1	D-219
N-Nitrosodimethylamine	--	nd
Chlordane	--	nd
Toxaphene	--	nd
PCB 1016	--	nd
PCB 1221	30	nd
PCB 1232	--	nd
PCB 1242	--	nd
PCB 1248	--	nd
PCB 1254	36	nd
PCB 1260	--	D-164
2-Chlorophenol	3.3	23-134
2-Nitrophenol	3.6	29-182
Phenol	1.5	5-112
2,4-Dimethylphenol	2.7	32-119
2,4-Dichlorophenol	2.7	39-135
2,4,6-Trichlorophenol	2.7	37-144
4-Chloro-3-methylphenol	3.0	22-147
2,4-Dinitrophenol	42	D-191
2-Methyl-4,6-dinotrophenol	24	D-181
Pentachlorophenol	3.6	14-176
4-Nitrophenol	2.4	D-132

and cannot be separated from diphenylamine. The preferred method of analysis for this analyte is Method 607.

Summary of method

35. An approximate 1-ℓ sample is extracted 3 times with methylene chloride at a pH greater than 11 and then acidified to a pH less than 2 and extracted 3 more times using a separatory funnel or continuous liquid-liquid extractor. The combined extract is dried and concentrated to 1 ml using a Kuderna-Danish concentrator and nitrogen. A portion of the concentrated extract is injected into a GC and analyzed by the mass spectrometer.

Equipment and operating conditions

36. The following equipment and operating conditions apply:

a. Gas chromatograph.

(1) Injection port and transfer line temperature: 250-300° C.

(2) Column: 30-m by 0.25-mm ID (or 0.32-mm ID) SE-54 bonded phase fused-silica capillary column (J&W Scientific DB-5 or equivalent). Helium carrier gas is set at 30 cm/sec. Hydrogen carrier gas can also be used.

(3) A sample volume of 1 to 2 µℓ is usually used.

(4) Temperature. Initially at 40° C for 4 min, then programmed at 10° C/min to 270° C and held there until benzo(g,h,i)-perylene has eluted.

b. Mass spectrometer. Scan from 35 to 450 atomic mass units (amu) every 1 to 2 sec with 70-V electron energy in the electron impact ionization mode. The mass spectrum obtained must meet the criteria listed in Table A17 for 50-ng decafluorotriphenyl phosphine (DFTPP) injected through the GC inlet.

Table A17

Decafluorotriphenyl phosphine Key Masses and Abundance Criteria, Method 625

Mass	M/Z Abundance Criteria
51	30-60% of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40-60% of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1 percent of mass 198
411	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

c. Data system. The MS should be interfaced to a data system capable of recording and storing all mass spectra generated during the chromatographic run. The computer software must be capable of searching for specific M/Z values and integrating their abundance.

Interferences and contamination

37. All reagents, glassware, solvents, water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the extractables analysis above the MDL for that parameter. Phthalates are some of the most common laboratory contaminants. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be particularly troublesome when high-level samples are followed by low-level ones. Matrix interferences can be especially difficult depending upon the nature of the sample as these are hard to eliminate.

Identification

38. To make a qualitative identification of a parameter, the following criteria must be met:

a. The primary and secondary M/Z values must maximize in the same or one full supectrum scan of each other.

b. The RT of the unknown must fall within ±30 sec of the standard.

c. The relative peak height of the M/Z values selected must be within ±20 percent of these values in the standard. Structural isomers of similar mass are very difficult to identify even with these criteria. Adequate chromatographic resolution must be accomplished to assure a good identification in this case.

39. Chemical ionization MS may be used in the identification process and can be quite useful when large amounts of interferences are present.

Quality assurance/quality control

40. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored.

b. The laboratory must spike and duplicate 5 percent of all samples on a continuing basis to evaluate data quality against the original control charts. These data should be added to the control charts periodically to update them. The spike value should be in the range of 1 to 5 times the value in the

samples. As an analyst becomes more proficient at an analysis, the tighter the ranges on the control chart will become.

c. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

d. The analyst must verify at the beginning of each shift that the established calibration curve is still valid through the analysis of 100-µg/ℓ check standard containing all parameters of interest. If any compounds fall outside the acceptance criteria of Table A18, the problem must be corrected and a reanalysis performed.

e. Any parameter result beyond the calibrated range must be diluted within range.

f. The laboratory must spike each sample analyzed with at least three of the surrogates listed in Table A19 and monitor the percent recovery. This is best accomplished by adding the surrogates to the initial samples to check precision and accuracy. The average percent R of the surrogates and their standard deviation are calculated. The recovery of the surrogates in each sample must fall within $R \pm 3\ SD$, or the sample must be reanalyzed.

g. All calculations should be calculated by the internal standard method. Suggested internal standards are listed in Table A19. The internal standard method best compensates for any instrument irregularities and aids in the identification by use of relative RTs.

h. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Method 8270, Semivolatile Organics by Capillary Column GC/MS

41. Method 8270 covers the analysis of the base neutral and acid extractable organic compounds listed in Table A20 in a variety of solid and liquid matrices by capillary column GC/MS. The method is applicable to the determination of most basic, neutral, and acidic organic compounds that are soluble in methylene chloride. A prerequisite is that the analyte elutes as a sharp peak from the recommended SE-54 bonded fused-silica capillary column.

42. Alpha-BHC, gamma-BHC, Endosulfan I and II, and endrin are subject to decomposition because of the basic extraction conditions and are best analyzed by Method 608. Hexachlorocyclopentadine is subject to thermal decomposition in the injection port of the GC and is preferably analyzed by Method 612. N-Nitrosodiphenylamine decomposes in the injection port and

Table A18

Quality Control Acceptance Criteria, Method 625

Compound Name	Test Conclusion µg/ℓ	Limits for SD*, µ/ℓ	Range for X,** µ/ℓ
Acenaphthene	100	27.6	60.1-132.3
Acenaphthylene	100	40.2	53.5-126.0
Aldrin	100	39.0	7.2-152.2
Anthracene	100	32.0	43.4-118.0
Benzo(a)anthracene	100	27.6	41.8-133.0
Benzo(b)fluoranthene	100	38.8	42.0-140.4
Benzo(k)fluoranthene	100	32.3	25.2-145.7
Benzo(a)pyrene	100	39.0	31.7-148.0
Benzo(g,h,i)perylene	100	58.9	D-195.0
Benzyl butyl phthalate	100	23.4	D-139.9
Gamma-BHC	100	31.5	41.5-130.6
Delta-BHC	100	21.6	D-100.0
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4
2-Chloronaphthalene	100	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7
Chrysene	100	48.3	44.1-139.9
4,4'-DDD	100	31.0	D-134.5
4,4'-DDE	100	32.0	19.2-119.7
4,4'-DDT	100	61.6	D-170.6
Dibenzo(a,h)anthracene	100	70.0	D-199.7
Di-n-butyl phthalate	100	16.7	8.4-111.0
1,2-Dichlorobenzene	100	30.9	48.6-112.0
1,3-Dichlorobenzene	100	41.7	16.7-153.9
1,4,-Dichlorobenzene	100	32.1	37.3-105.7
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5
Dieldrin	100	30.7	44.3-119.3
Diethyl phthalate	100	26.5	D-100.0
Dimethyl phthalate	100	23.2	D-100.0
2,4-Dinitrotoluene	100	21.8	47.5-126.9
2,6-Dinitrotoluene	100	29.6	68.1-136.7
Di-n-octyl phthalate	100	31.4	18.6-131.8
Endosulfan sulfate	100	16.7	D-103.5
Endrin aldehyde	100	32.5	D-188.8
Fluoranthene	100	32.8	42.9-121.3
Fluorene	100	20.7	71.6-108.4
Heptachlor	100	37.2	D-172.2
Heptachlor epoxide	100	54.7	70.9-109.4

(Continued)

* SD = standard deviation for four recovery measurements.

** X = average recovery for four recovery measurements; D = detected, result must be greater than zero.

Table A18 (Concluded)

Compound Name	Test Conclusion ug/ℓ	Limits for SD, μ/ℓ	Range for X, μ/ℓ
Hexachlorobenzene	100	24.9	7.8-141.5
Hexachlorobutadiene	100	26.3	37.8-102.2
Hexachlorethane	100	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9
Isophorone	100	63.3	46.6-180.2
Naphthalene	100	30.1	35.6-119.6
Nitrobenzene	100	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9
PCB-1260	100	54.2	19.3-121.0
Phenanthrene	100	20.6	65.2-108.7
Pyrene	100	25.2	69.6-100.0
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2
4-Chloro-3-methylphenol	100	37.2	40.8-127.9
2-Chlorophenol	100	28.7	36.2-120.4
2,4-Dichlorophenol	100	26.4	52.5-121.7
2,4-Dimethylphenol	100	26.1	41.8-109.0
2,4-Dinitrophenyl	100	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0
2-Nitrophenol	100	35.2	45.0-166.7
4-Nitrophenol	100	47.2	13.0-106.5
Pentachlorophenol	100	48.9	38.1-151.8
Phenol	100	22.6	16.6-100.0
2,4,6-Trichlorophenol	100	31.7	52.4-129.2

Table A19

Suggested Internal and Surrogate Standards, Method 625

Base/Neutral Fraction	Acid Fraction
Aniline-d_5	2-Fluorophenol
Anthracene-d_{10}	Pentafluorophenol
Benzo(a)anthracene-d_{12}	Phenol-d_5
4,4'-Dibromobiphenyl	2-perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene-d_8	
Nitrobenzene-d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

Table A20

Practical Quantitation Limits for Semivolatile Organics and Percent Recovery,* Method 8270

Compound Name	PQL** Ground Water µg/ℓ	PQL** Low Soil/Sediment µg/kg	Range P, P_s,† %
Phenol	10	660	5-112
bis(2-Chloroethyl) ether	10	660	12-158
2-Chlorophenol	10	660	23-134
1,3-Dichlorobenzene	10	660	D-172
1,4-Dichlorobenzene	10	660	20-124
Benzyl alcohol	20	1,300	nd
1,2-Dichlorobenzene	10	660	32-129
2-Methylphenol	10	660	nd
bis(2-Chloroisopropyl) ether	10	660	36-166
4-Methylphenol	10	660	nd
N-Nitroso-di-n-propylamine	10	660	D-230
Hexachloroethane	10	660	40-113
Nitrobenzene	10	660	35-180
Isophorone	10	660	21-196
2-Nitrophenol	10	660	29-182
2,4-Dimethylphenol	10	660	32-119
Benzoic acid	50	3,300	nd
bis(2-Chloroethoxy)methane	10	660	33-184
2,4-Dichlorophenol	10	660	nd
1,2,4-Trichlorobenzene	10	660	44-142
Naphthalene	10	660	21-133
4-Chloroaniline	20	1,300	nd
Hexachlorobutadiene	10	660	24-116
4-Chloro-3-methylphenol	20	1,300	22-147
2-Methylnaphthalene	10	660	nd
Hexachlorocyclopentadiene	10	660	nd
2,4,6-Trichlorophenol	10	660	37-144
2,4,5-Trichlorophenol	10	660	nd
2-Chloronaphthalene	10	660	60-118
2-Nitroaniline	50	3,300	nd
Dimethyl phthalate	10	660	D-112
Acenaphthylene	10	660	33-145
3-Nitroaniline	50	3,300	nd
Acenaphthene	10	660	47-145
2,4-Dinitrophenol	50	3,300	D-191
4-Nitrophenol	50	3,300	D-132
Dibenzofuran	10	660	nd

(Continued)

* From 40 CFR Part 136 for Method 625, calculated using a 20-µg/ℓ check sample of each parameter.

** Based on wet weight.

† P, P_s = Percent recovery measured; D = detected, result must be greater than zero.

Table A20 (Concluded)

Compound Name	PQL Ground Water µg/ℓ	PQL Low Soil/Sediment µg/kg	Range P, P_s, %
2,4-Dinitrotoluene	10	660	39-139
2,6-Dinitrotoluene	10	660	50-158
Diethyl phthalate	10	660	D-114
4-Chlorophenyl phenyl ether	10	660	25-158
Fluorene	10	660	59-121
4-Nitroaniline	50	3,300	nd
4,6-Dinitro-2-methylphenol	50	3,300	nd
N-Nitrosodiphenylamine	10	660	nd
4-Bromophenyl phenyl ether	10	660	53-127
Hexachlorobenzene	10	660	D-152
Pentachlorophenol	50	3,300	14-176
Phenanthrene	10	660	54-120
Anthracene	10	660	27-133
Di-n-butyl phthalate	10	660	1-118
Fluoranthene	10	660	26-137
Pyrene	10	660	52-115
Butyl benzyl phthalate	10	660	D-152
3,3'-Dichlorobenzidine	20	1,300	D-262
Benzo(a)anthracene	10	660	33-143
bis(2-Ethylhexyl) phthalate	10	660	8-158
Chrysene	10	660	17-168
Di-n-octyl phthalate	10	660	4-146
Benzo(b)fluoranthene	10	660	24-159
Benzo(k)fluoranthene	10	660	11-162
Benzo(a)pyrene	10	660	17-163
Indeno(1,2,3-cd)pyrene	10	660	D-171
Dibenz(a,h)anthracene	10	660	nd
Benzo(g,h,i)perylene	10	660	D-219

cannot be separated from diphenylamine. The preferred method of analysis for this analyte is Method 607.

43. Several phenolic and aniline compounds are subject to erratic chromatographic behavior, especially when the gas chromatographic system is contaminated or has active sites in the inlet system, column, transfer lines, etc.

44. In Table A20 the PQL for each evaluated semivolatile organic compound is listed. These PQLs should be obtainable depending on the nature and level of interferences present in the matrix.

Summary of method

45. The sample is appropriately liquid-liquid, soxhlet, or sonicatively extracted. Some nonaqueous wastes require only solvent dilution. The extract

is dried and concentrated to 1-ml using a Kuderna-Danish concentrator and nitrogen. A portion of the concentrated extract is injected into a GC and analyzed by the MS.

Equipment and operating conditions

46. The following equipment and operating conditions apply:

a. Gas chromatograph.

(1) Injection port and transfer line to temperature: 250° to 300° C.

(2) Column: 30 m by 0.25-mm-ID (or 0.32-mm-ID) SE-54 bonded phase fused-silica capillary column (J&W Scientific DB-5 or equivalent). Helium carrier gas is set at 30 cm/sec. Hydrogen carrier gas can also be used.

(3) A sample volume of 1 to 3 µℓ is usually used.

(4) Temperature: Initially at 40° C for 4 min, and then programmed at 10° C/min to 270° C and held there until benzo[g,h,i]perylene has eluted.

b. Mass spectrometer. Scan from 35 to 500 amu every 1 sec or less with 70-V electron energy in the electron impact ionization mode. The mass spectrum obtained must meet the criteria listed in Table A21 for 50-ng DFTPP injected through the GC inlet.

Table A21

Decafluorotriphenyl phosphine Key Ions and Ion Abundance Criteria, Method 8270

Mass	M/Z Abundance Criteria
51	30-60% of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40-60% of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1 percent of mass 198
411	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

c. Data system. The MS should be interfaced to a data system capable of recording and storing all mass spectra generated during the chromatographic run. The computer software must be capable of searching specific M/Z values and integrating their abundance. The most recent version of the EPA/NIH Mass Spectral Library should be available to facilitate the

identification of any unknown compounds present in the gas chromatographic run if requested.

Interferences and contamination

47. All reagents, glassware, solvents, water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the extractables analysis above the PQL for that parameter. Phthalates are some of the most common laboratory contaminants. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be particularly troublesome when high-level samples are followed by low-level ones.

48. Matrix interferences can be especially difficult depending upon the nature of the sample as these are hard to eliminate.

Identification

49. Qualitative. To make a qualitative identification of a parameter the following criteria must be met:

a. The primary and secondary M/Z values must maximize in the same or one full spectrum scan of each other.

b. The unknown RRT must agree within ±0.06 RRT units of the RRT of the compound in the standard run.

c. The relative peak intensities of the specified M/Z values must be within ±20 percent of those values in the standard.

d. All ions present in the standard mass spectra above 10-percent relative intensity to the base peak must be present in the sample component.

50. An EPA/NIH library search may be requested of any unknown components present in the sample. Guidelines for the evaluation of a tentative identification of the unknown sample component are:

a. Relative intensities of the major M/Z values in the library spectrum above 10 percent relative to the base peak should be present.

b. Relative intensities of these major ions should agree within ±20 percent.

c. Molecular ions that are present in the library spectrum should be in the sample component.

After the computer search, the mass spectral interpretation specialist should evaluate the resultant tentative identification.

51. Quantitative. To make a quantitative identification of a parameter, the following criteria must be met:

a. Identified compound. Quantification of the identified sample compound must be by the internal standard technique. The recommended internal standards are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The internal standards with their corresponding analytes are listed in Table A22. Liquid samples are normally reported in µg/ℓ. Sediment samples are usually reported in µg/kg on a dry-weight basis, while sludges and wastes are reported on a wet-weight basis.

b. Tentatively identified. Tentatively identified sample components can be estimated by the internal standard approach using the nearest RT internal standard that is free of interferences. The RF is assumed to be 1.

Quality assurance/quality control

52. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored.

b. The laboratory must spike and duplicate 5 percent of all samples on a continuing basis to evaluate data quality against the original control charts. These data should be added to the control charts periodically to update them. The spike value should be in the range of 1 to 5 times the value in the sample. As an analyst becomes more proficient at an analysis, the tighter the ranges on the control chart will become.

c. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

d. The analyst must verify at the beginning of each shift that the analytical system is operating properly through the analysis of the SPCCs. The SPCCs are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. The SPCCs are checked for an average minimum RF of 0.050. Lower RFs for these compounds will typically result from contaminated and/or active sites in the GC inlet, GC column, GC transfer line to the MS, and the jet separator if present.

e. After the SPCCs are checked, the analyst must verify that the established 5-point calibration curve is still valid through the analysis of the CCCs. The CCCs are 1,4-dichlorobenzene, hexachlorobutadiene, N-nitroso-di-n-prophylamine, acenaphthene, fluoranthene, di-n-octylphthalate, benzo(a)pyrene, phenol, 2-nitrophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol. The percent difference for each CCC cannot exceed 30 percent with 20 percent used as a warning limit. The RT of the internal standard

Table A22

Semivolatile Internal Standards with Corresponding Analytes Assigned to Quantitation, Method 8270

1,4-Dichlorobenzene-d_4	Napthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Aniline	Acetophenone	Acenaphthene	4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Benzyl alcohol	Benzoic acid	Accenaphthylene	Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy) methane	1-Chloronaphthalene	4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i) perylene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene	Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether	4,6-Dinitro-2 methylphenol	Chrysene	Dibenz(a,j)acridine
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran	Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h) anthracene
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate	1,2-Diphenylhydrazine	p-Dimethylamionazobenzene	7,12-Dimethylbenz(a)anthracene
1,2-Dichlorobenzene	, -Dimethyl phenethylamine	Dimethyl phthalate	Fluoranthene	Pyrene	Di-n-octyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol	Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd) pyrene
2-Fluorophenol (surr.)*	Hexachlorobutadiene	2,4-Dinitrotoluene	N-Nitrosodiphenylamine		3-Methylcholanthraene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene	Pentachlorophenol		
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene	Pentachloronitrobenzene		
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)	Phenacetin		
4-Methylphenol	Nitrobenzene	Hexachlorocyclo pentadiene	Phenanthrene		
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine	Pronamide		
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine			
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline			
Phenol-d_6 (surr.)	N-Nitrosopiperdine	3-Nitroaniline			
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline			
		4-Nitrophenol			
		Pentachlorobenzene			
		1,2,4,5-Tetrachlorobenzene			
		2,3,4,6-Tetrachlorophenol			
		2,4,6-Tribromophenol (surr.)			
		2,4,6-Trichlorophenol			
		2,4,5-Trichlorophenol			

* (surr.) = surrogate.

should not change by more than 30 sec from any previous CCC checks. When this occurs, there is likely to be a chromatographic problem.

f. Any parameter result beyond the calibrated range must be diluted within range.

g. The laboratory must spike each sample analyzed with the six surrogate compounds listed in Table A23. After a minimum of 30 samples of the sample matrix are analyzed, a control chart based on percent R of each surrogate and their standard deviation must be prepared. The R for each surrogate should fall within $R \pm 3$ SD, or the sample must be reanalyzed. Each $R \pm 3$ SD surrogate range should fall within the guideline of Table A23.

Table A23

Surrogate Spike Recovery Limits for Water and Soil/Sediment Samples, Method 8270

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

h. The laboratory should on a continuing basis analyze external QC blind samples to check method performance.

Method 608, Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)

53. Method 608 covers the analysis of the organochlorine pesticides and PCBs listed in Table A24 by GC with election capture detection. In Table A24 the MDL for each parameter is listed. These MDLs should be obtainable depending on the nature and level of interferences present in the water sample.

Summary of method

54. An approximate 1-ℓ sample is extracted 3 times with methylene chloride using a separatory funnel or continuous liquid-liquid extractor. The extract is dried, concentrated, solvent exchanged with hexane, and

Table A24

Method Detection Limits and Percent Recovery, Method 608

Compound Name	Method Detection Limit, µg/ℓ	Range for P, P_s,* %
Alpha-BHC	0.003	37-134
Gamma-BHC	0.004	32-127
Beta-BHCC	0.006	17-147
Heptachlor	0.003	34-111
Delta-BHC	0.009	19-140
Aldrin	0.004	42-122
Heptachlor expoxide	0.083	37-142
Endosulfan I	0.014	45-153
4,4'-DDE	0.004	30-145
Dieldrin	0.002	36-146
Endrin	0.006	30-147
4,4'-DDD	0.011	31-141
Endosulfan II	0.004	D-202
4,4'-DDT	0.012	25-160
Endrin aldehyde	0.023	nd
Endosulfan sulfate	0.066	26-144
Chlordane	0.014	45-119
Toxaphene	0.24	41-126
PCB-1016	nd	50-114
PCB-1221	nd	15-178
PCB-1232	nd	10-215
PCB-1242	0.065	39-150
PCB-1248	nd	38-158
PCB-1254	nd	29-131
PCB-1260	nd	8-127

* P, P_s = percent recovery measured; D = detected, result must be greater than zero; nd = not determined.

reconcentrated to 10 ml using a Kuderna-Danish concentrator. A portion of the extract is injected into a GC equipped with an electron capture detector.

Equipment and operating conditions

55. The following equipment and operation conditions apply:

a. Gas chromatograph conditions.

(1) Column 1: 6-ft-long by 4-mm-ID glass column packed with 1.5-percent SP-2250/1.95-percent SP-2401 coated on 100- to 120-mesh Supelcoport. The column temperature is held isothermally at 200° C, except for the analysis of PCB-1016 through PCB-1248, which should be run at 160° C.

(2) Column 2: 6-ft-long by 4-mm-ID glass column packed with 3 percent OV-1 coated on 100- to 120-mesh Supelcoport. The column temperature is held isothermally at 200° C for pesticide analysis, at 140° C for PCB-1221 and 1232, and at 170° C for PCB-1016 and 1242 through 1260.

(3) For the electron capture detector, 5-percent methane/ 95-percent argon carrier gas is set to a 60-ml/min flow rate.

(4) A sample volume of 2 to 5 μℓ is usually used.

(5) Microcoulometric or electrolytic conductivity detection may be used instead of electron capture detection.

b. Data system. A data system is preferred for the measuring of peak areas or heights and retention times from the point of injection.

Interferences and contamination

56. All reagents, glassware, solvents, reagent water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the pesticide or PCB analysis above the MDL for that parameter. Phthalates are some of the most common laboratory contaminates. Contamination due to phthalate interference can be eliminated by the use of microcoulometric or electrolytic conductivity detection instead of using electron capture detection. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be be troublesome when high-level samples are followed by low-level ones. Matrix interferences can be especially difficult depending upon the nature of the sample. Sulfur is one of the most common interferents. It can be eliminated by shaking 1 ml of extract with several drops of triple distilled mercury. Florisil column cleanup is another means of eliminating interferences from the sample extract. It is used mainly for eliminating polar interferences and for fractionating the analytes into select fractions that can aid the parameter identification process.

Identification and quantification

57. Identification and quantification are usually accomplished by the external standard procedure. By this approach, the analyst matches the RT of the peak(s) present in the standards with peaks in the sample. Identifications based on RT should take into account any RT changes occurring during the analysis of standards analyzed before and after the samples. For example, 2 SD are used as a warning limit, and 3 SD are used as an outmost limit in the calculation of RT windows for identification.

58. Quantitation is based on area response of the detected parameter versus concentration derived from a 3-point calibration curve. For multicomponent mixtures (chlordane, toxaphene, and PCBs), peak height or area of each identified peak in the chromatogram is summed as a total response versus standard total response.

59. When the external standard approach is used, it is particularly important to confirm all positive identifications on a GC column of differing polarity from the main analytical column. This will add more creditability to the identification.

Quality assurance/quality control

60. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. The resultant precision and accuracy data must fall within the guidelines of Table A25.

b. The laboratory must spike 10 percent of all samples on a continuing basis to evaluate data quality against the original control charts. After the analysis of five spike wastewater samples, the accuracy can be expressed in control charts as average recovery ±2 SD to monitor data quality. The spike value should be in the range of 1 to 5 times the value in the samples.

c. The laboratory must analyze a check standard sample containing all parameters at a frequency of 10 percent of the samples analyzed to verify that the measurement system is in control. The resultant concentration for the check sample is in the range of 2 to 10 µg/ℓ for single component pesticides and 50 µg/ℓ for the multicomponent parameters. The QC guidelines in Table A25 must be met.

d. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

e. The analyst must verify at the beginning of each shift that the established calibration curve is valid by the analysis of one or more calibration standards. The response should be within 15 percent of the original response.

f. Any parameter result beyond the calibrated range must be diluted within range.

Table A25

Quality Control Acceptance Criteria, Method 608

Compound Name	Test Conc. µg/ℓ	Limit for SD,* µg/ℓ	Range for X,** µg/ℓ
Aldrin	2.0	0.42	1.08- 2.24
Alpha-BHC	2.0	0.48	0.98- 2.44
Beta-BHC	2.0	0.64	0.78- 2.60
Delta-BHC	2.0	0.72	1.01- 2.37
Gamma-BHC	2.0	0.46	0.86- 2.32
Chlordane	50	10.0	27.6 -54.3
4,4'-DDD	10	2.8	4.8 -12.6
4,4'-DDE	2.0	0.55	1.08- 2.60
4,4'-DDT	10	3.6	4.6 -13.7
Dieldrin	2.0	0.76	1.15- 2.49
Endosulfan I	2.0	0.49	1.14- 2.82
Endosulfan II	10	6.1	2.2 -17.1
Endosulfan sulfate	10	2.7	3.8 -13.2
Endrin	10	3.7	5.1 -12.6
Heptachlor	2.0	0.40	0.86- 2.00
Heptachlor epoxide	2.0	0.41	1.13- 2.63
Toxaphene	50	12.7	27.8 -55.6
PCB-1016	50	10.0	30.5 -51.5
PCB-1221	50	24.4	22.1 -75.2
PCB-1232	50	17.9	14.0 -98.5
PCB-1242	50	12.2	24.8 -69.6
PCB-1248	50	15.9	29.0 -70.2
PCB-1254	50	13.8	22.2 -57.9
PCB-1260	50	10.4	18.7 -54.9

* SD = standard deviation of four recovery measurements.
** X = average recovery for four recovery measurements.

g. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Method 8080, Organochlorine Pesticides and PCBs

61. Method 8080 covers the analysis of the organochlorine pesticides and PCBs listed in Table A26 in a variety of liquid and solid matrices by GC with either electron capture or halogen-specific detection. In Table A26 the MDL for each parameter in reagent water is listed. In Table A27 the PQL for other matrix types is listed. The PQL for each matrix usually depends more on the level of interferences than on instrumental limitations.

Table A26

Method Detection Limits and Percent Recovery,* Method 8080

Compound Name	Method Detection Limit, µg/ℓ	Range for P, P_s,** %
Aldrin	0.004	42-122
-BHC	0.003	37-134
-BHC	0.006	17-147
-BHC	0.009	19-140
-BHC(Lindane)	0.004	32-127
Chlordane (technical)	0.014	45-119
4,4'-DDD	0.011	31-141
4,4'-DDE	0.004	30-145
4,4'-DDT	0.012	25-160
Dieldrin	0.002	36-146
Endosulfan I	0.014	45-153
Endosulfan II	0.004	D-202
Endosulfan sulfate	0.066	26-144
Endrin	0.006	30-147
Endrin aldehyde	0.023	nd
Heptachlor	0.003	34-111
Heptachlor epoxide	0.083	37-142
Methoxychlor	0.176	nd
Toxaphene	0.24	41-126
PCB-1016	nd	50-114
PCB-1221	nd	15-178
PCB-1232	nd	10-215
PCB-1242	0.065	39-150
PCB-1248	nd	38-158
PCB-1254	nd	29-131
PCB-1260	nd	8-127

* Criteria based on 40 CFR Part 136 for Method 608.

** P,P_s = Percent recovery measured; D = detected, result must be greater than zero; nd = not determined.

Summary of method

62. The sample is appropriately liquid-liquid, soxhlet, or sonicatively extracted. Some nonaqueous wastes require only solvent dilution. The extract is dried, concentrated, solvent exchanged with hexane, and reconcentrated to 10 ml using a Kuderna-Danish concentrator. A portion of the extract (2 to 5 µℓ) is injected into a GC equipped with an electron capture or halogen specific detector.

Table A27

Determination of PQL for Various Matrices,* Method 8080

Matrix	Factor**
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Nonwater miscible waste	100,000

* Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

** PQL = [MDL (Table A26)] × [Factor (Table A27)]. For nonaqueous samples, the factor is on a wet-weight basis.

Equipment and operating conditions

63. The following equipment and operating conditions apply:

a. Gas chromatograph conditions.

(1) Column 1: 6-ft-long by 4-mm-ID glass column packed with 1.5-percent SP-2250/1.95-percent SP-2401 coated on 100 to 120 mesh Supelcoport. The column temperature is held isothermally at 200° C, except for the analysis of PCB-1016 through PCB-1248, which should be run at 160° C.

(2) Column 2: 6-ft-long by 4-mm-ID glass column packed with 3 percent OV-1 coated on 100- to 120-mesh Supelcoport. The column temperature is held isothermally at 200° C for pesticide analysis, at 140° C for PCB-1221 and 1232, and at 170° C for PCB-1016 and 1242 through 1260.

(3) For the electron capture detector, 5-percent methane/95-percent argon carrier gas is set to a 60-ml/min flow rate.

(4) A sample volume of 2 to 5 µℓ is usually used.

(5) Microcoulometric or electrolytic conductivity detection may be used instead of electron capture detection.

b. Data system. A data system is preferred for the measuring of peak areas and RT from the point of injection.

Interferences and contamination

64. All reagents, glassware, solvents, reagent water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the pesticide or PCB analysis above the MDL for that parameter. Phthalates are some of the most common laboratory contaminants. Contamination due to phthalate interference can be eliminated by the use of microcoulometric or electrolytic conductivity detection instead of using electron capture

detection. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be troublesome when high-level samples are followed by low-level ones. Matrix interferences can be especially difficult depending upon the nature of the sample. Sulfur is one of the most common interferents. It can be eliminated by shaking 1 ml of extract with several drops of triple distilled mercury. Florisil column cleanup is another means of eliminating interferences from the sample extract. It is used mainly for eliminating polar interferences and fractionating the analytes into select fractions that can aid the parameter identification process.

Identification and quantification

65. Identification and quantification are usually accomplished by the external standard procedure. By this approach the analyst matches the RT of the peak(s) present in the standards with peaks in the sample. Identifications based on RT should take into account any RT changes occurring during the analysis of standards analyzed before and after the samples. For example, 2 SD are used as a warning limit, and 3 SD are used as an outmost limit.

66. Quantitation is based on area response of the detected parameter versus concentration derived from a 5-point calibration curve. For multicomponent mixtures (chlordane, toxaphene, and PCBs), peak height or area of each identified peak in the chromatogram is summed as a total response versus standard total response.

67. When the external standard approach is used, it is particularly important to confirm all positive identifications on a GC column of differing polarity from the main analytical column. This will add more creditability to the identification.

Quality assurance/quality control

68. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points.

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. The resultant precision and accuracy data must fall within the guidelines of Table A28.

Table A28

Quality Control Acceptance Criteria,* Method 8080

Compound Name	Test Conc. µg/ℓ	Limit for SD,** µg/ℓ	Range for X,† µg/ℓ
Aldrin	2.0	0.42	1.08- 2.24
Alpha-BHC	2.0	0.48	0.98- 2.44
Beta-BHC	2.0	0.64	0.78- 2.60
Delta-BHC	2.0	0.72	1.01- 2.37
Gamma-BHC	2.0	0.46	0.86- 2.32
Chlordane	50	10.0	27.6 -54.3
4,4'-DDD	10	2.8	4.8 -12.6
4,4'-DDE	2.0	0.55	1.08- 2.60
4,4'-DDT	10	3.6	4.6 -13.7
Dieldrin	2.0	0.76	1.15- 2.49
Endosulfan I	2.0	0.49	1.14- 2.82
Endosulfan II	10	6.1	2.2-17.1
Endosulfan sulfate	10	2.7	3.8-13.2
Endrin	10	3.7	5.1-12.6
Heptachlor	2.0	0.40	0.86- 2.00
Heptachlor epoxide	2.0	0.41	1.13- 2.63
Toxaphene	50	12.7	27.8 -55.6
PCB-1016	50	10.0	30.5 -51.5
PCB-1221	50	24.4	22.1 -75.2
PCB-1232	50	17.9	14.0 -98.5
PCB-1242	50	12.2	24.8 -69.6
PCB-1248	50	15.9	29.0 -70.2
PCB-1254	50	13.8	22.2 -57.9
PCB-1260	50	10.4	18.7 -54.9

* Criteria based on 40 CFR Part 136 for Method 608.
** SD = standard deviation of four recovery measurements.
† X = average recovery for four recovery measurements.

b. The laboratory must analyze a reagent blank, matrix spike, and matrix spike duplicate/duplicate as a minimum for each analytical batch up to 20 samples. The spike value should be in the range of 1 to 5 times the value in the samples. The organochlorine pesticide matrix spiking solution should contain lindane, heptachlor, and aldrin at 0.2 µg/ℓ and dieldrin, endrin, and 4,4'DDT at 0.5 µg/ℓ. After the analysis of five spiked samples (same matrix type) the accuracy can be expressed in control charts as average recovery ±2 SD to monitor data quality.

c. The laboratory must routinely analyze a check standard sample containing all parameters of interest. The need for check standard sample analysis increases with the complexity of the sample matrix and the number of analytes present. If an

analyte spike value falls outside the range of recoveries (from the QC chart, item b), a check standard sample must be analyzed. The concentration for the check sample concentrate is in the range of 2 to 10 µg/ml for single component pesticides, and 50 µg/ml for the multicomponent parameters. The QC guidelines in Table A28 must be met.

d. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

e. The analyst must verify at the beginning of each shift that the established calibration curve is valid by the analysis of one or more calibration standards. The response should be within 15 percent of the original response.

f. A midlevel calibration standard should be run after each group of 10 samples to verify the initial calibration.

g. The surrogates recommended in organochlorine pesticide analysis are dibutylchlorendate (DBC) and 2,4,5,6-tetrachloro-meta-xylene. Each sample, blank, and spike must contain the surrogates. Once a minumum of 30 samples of the same matrix type have been analyzed, the average percent recovery (P) and standard deviation of the percent recovery for each surrogate can be calculated. The method performance for the surrogates should be calculated as $P \pm 3\ SD$. At a minimum the DBC recovery should be within 24 to 154 percent for water and 20 to 150 percent for soil.

h. Before calibration, the GC system should be checked by monitoring for the degradation products of 4,4'DDT (4,4'DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). Corrective action must be taken before sample analysis if the degradation of endrin or 4,4'-DDT exceeds 20 percent.

i. Any parameter result beyond the calibrated range must be diluted within range.

j. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Method 8150, Chlorinated Herbicides

69. Method 8150 covers the analysis of the chlorinated acid herbicides listed in Table A29 in a variety of liquid and solid matrices by GC with either electron capture, microcoulometric, or electrolytic conductivity detection. In Table A29 the MDL for each parameter in reagent water is listed. In Table A30 the PQL for other matrix types is listed. The PQL for each matrix usually depends more on the level of interferences than on instrumental limitations.

Table A29

Detection Limits for Chlorinated Herbicides, Method 8150

Compound	MDL, µg/ℓ
2,4-D	1.2
2,4-DB	0.91
2,4,5-T	0.20
2,4,5-TP (Silvex)	0.17
Dalapon	5.8
Dicamba	0.27
Dichloroprop	0.65
Dinoseb	0.07
MCPA	249
MCPP	192

Table A30

Determination of PQL for Various Matrices,* Method 8150

Matrix	Factor**
Ground Water	10
Low-level soil by sonication with GCP cleanup	670
High-level soil and sludges by sonication	10,000
Nonwater miscible waste	100,000

* Sample PQLs are highly matrix-dependent. The PQLS listed herein are provided for guidance and may not always be achievable.

** PQL = [MDL (Table A29)] × [Factor (Table A30)]. For non-aqueous samples, the factor is on a wet-weight basis.

Summary of method

70. The sample is pH adjusted to 2. Solid samples are extracted with acetone/diethyl ether and liquids with diethyl ether. The acetone from the solids extract is eliminated by acid water washing of the extract. The extracts are basic hydrolyzed followed by solvent extraction (to eliminate interferences). The basic hydrolyzate is acidified to pH 2, diethyl ether extracted, and concentrated. The concentrated extract is methyl esterified using diazomethane. A portion of the extract (2 to 5 µℓ) is injected into a

GC equipped with an electron capture or other appropriate detector. The methylated herbicides are reported as their acid equivalents.

Equipment and operating conditions

71. The following equipment and operating conditions apply:

a. Gas chromatograph conditions for electron capture detection.

(1) Column 1a: 1.8-m by 4-mm-ID glass column packed with 1.5-percent SP-2250/1.95-percent SP-2401 coated on 100- to 120-mesh Supelcoport. The column temperature is held isothermally at 185° C.

(2) Column 1b: 1.8-m by 4-mm-ID glass column packed with 1.5-percent SP-2250/1.95-percent SP-2401 coated on 100- to 120-mesh Supelcoport. The column temperature is held at 140° C for 6 min followed by a 10° C/min program to 200° C and held until the analysis is complete.

(3) Column 2: 1.8-m by 4-mm-ID glass column packed with 5-percent OV-210 coated on 100- to 120-mesh Gas Chrom Q. The column temperature is held isothermally at 185° C.

(4) Column 3: 1.98-m by 2-mm-ID glass column packed with 0.1-percent SP-1000 coated on 80- to 100-mesh Carbopac C. The column temperature is programmed 10° C/min from 100° to 150° C and held until the analysis is complete.

(5) For columns 1a, 1b, and 2, the 5-percent methane/ 95-percent argon carrier gas flow rate is set at 70 ml/min and for column 3, the nitrogen carrier gas flow rate is set at 25 ml/min.

(6) A sample volume of 2 to 5 µl is usually used.

(7) The recommended gas chromatographic columns that are used for the indicated analyte are listed in Table A31.

(8) Microcoulometric or electrolytic conductivity detection may be used instead of electron capture detection.

Table A31

Recommended Gas Chromatographic Columns, Method 8150

Parameter	Column
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

b. Data system: A data system is preferred for the measuring of peak areas or heights and RTs from the point of injection.

Interferences and contamination

72. All reagents, glassware, solvents, reagent water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the herbicide analysis above the MDL or PQL for that parameter. The acidification, alkaline hydrolysis, and subsequent extraction of the basic solution remove many base neutral compounds that might interfere with the electron capture analysis of the herbicides. Potentially, any acidic or chlorinated acidic organic compound might interfere with this analysis. Particular care must be exercised to treat all glassware, glass wool, and sodium sulfate with acid to give them acid character as the acid herbicide recovery can be diminished by basic character. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be troublesome when high-level samples are followed by low-level ones. Matrix interferences can be especially difficult depending on the nature of the sample. Florisil and silica gel column cleanup are a means of eliminating polar interferences and fractionating the analytes into select fractions that can aid the parameter identification process.

Identification and quantification

73. Identification and quantification are usually accomplished by the external standard procedure. By this approach, the analyst matches the RT of the peak(s) present in the standards with peaks in the sample. Identifications based on RT should take into account any RT changes occurring during the analysis of standards analyzed before and after the samples. For example, 2 SD are used as a warning limit, and 3 SD are used as an outmost limit in the calculation of RT windows for identification.

74. Quantitation is based on area or height response of the detected parameter versus concentration derived from a 5-point calibration curve. When the external standard approach is used, it is particularly important to confirm all positive identifications on a GC column of differing polarity from the main analytical column. This will add more creditability to the identification.

Quality assurance/quality control

75. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. The resultant precision and accuracy data must fall within the guidelines of Table A25.

b. The laboratory must analyze a reagent blank, matrix spike, and matrix spike duplicate/duplicate as a minimum for each analytical batch up to 20 samples. The spike value should be in the range of 1 to 5 times the value in the samples. After the analysis of five spiked samples (same matrix type), the accuracy can be expressed in control charts as average recovery ±2 SD to monitor data quality.

c. The laboratory must routinely analyze a check standard sample containing all parameters of interest. The need for check standard sample analysis increases with the complexity of the sample matrix and the number of analytes present. If an analyte spike value falls outside the range of recoveries (from the QC chart, item b) a check standard sample must be analyzed. The concentration for the check sample concentrate is 1,000 times more concentrated than the selected concentrations. The QC guidelines in Table A32 must be met.

d. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

e. The analyst must verify at the beginning of each shift that the established calibration curve is valid by the analysis of one or more calibration standards. The response should be within 15 percent of the original response.

f. A midlevel calibration standard should be run after each group of 10 samples to verify the initial calibration.

g. The surrogates recommended in herbicide analysis are one or two herbicides that are not expected to be present in the sample. Each sample, blank, and spike must contain the surrogates. Once a minimum of 30 samples of the same matrix type have been analyzed, the average percent R and standard deviation of the percent recovery for each surrogate can be calculated. The method performance for the surrogates should be calculated at $R \pm 3$ SD .

h. Any parameter result beyond the calibrated range must be diluted within range.

i. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.

Table A32

Single Operator Accuracy and Precision,* Method 8150

Parameter	Sample Type**	Spike µg/ℓ	Recovery %	Standard Deviation %
2,4-D	DW	10.9	75	4
	MW	10.1	77	4
	MW	200	65	5
Dalapon	DW	23.4	66	8
	MW	23.4	96	13
	MW	468	81	9
2,4-DB	DW	10.3	93	3
	MW	10.4	93	3
	MW	208	77	6
Dicamba	DW	1.2	79	7
	MW	1.1	86	9
	MW	22.2	82	6
Dichlorprop	DW	10.7	97	2
	MW	10.7	72	3
	MW	213	100	2
Dinoseb	MW	0.5	86	4
	MW	102	81	3
MCPA	DW	2,020	98	4
	MW	2,020	73	3
	MW	21,400	97	2
MCPP	DW	2,080	94	4
	MW	2,100	97	3
	MW	20,440	95	2
2,4,5,-T	DW	1.1	85	6
	MW	1.3	83	4
	MW	25.5	78	5
2,4,5-TP	DW	1.0	88	5
	MW	1.3	88	4
	MW	25.0	72	5

* Data obtained from EPA Method 615.
** DW = reagent water; MW = municipal water.

Method 8100, Polynuclear Aromatic Hydrocarbons

76. Method 8100 covers the analysis of the polynuclear aromatic hydrocarbons (PAH) listed in Table 33 in a variety of liquid and solid matrices by GC with flame ionization detection. This method cannot separate the following pairs of aromatic hydrocarbons: phenanthrene and anthracene; chrysene and benzo(a)anthracene; benzo(b)fluorantheneand benzo(k)fluoranthene; and

Table A33

Polynuclear Aromatic Hydrocarbons, Method 8100

Compound	Compound
Acenaphthene	Acenaphthylene
Anthracene	Benzo(a)anthracene
Benzo(a)pyrene	Benzo(b)fluoranthene
Benzo(j)fluoranthene	Benzo(k)fluoranthene
Benzo(g,h,i)perylen	Chrysene
Dibenz(a,h)acridine	Dibenzo(a,j)acridine
Dibenzo(a,h)anthracene	7H-Dibenzo(c,g)carbazole
Dibenzo(a,e)pyrene	Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene	Fluoranthene
Fluorene	Ideno(1,2,3-cd)pyrene
3-Methylcholanthrene	Naphthalene
Phenanthrene	Pyrene

dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene through the use of packed column GC. These PAHs might be adequately resolved through the use of an optional capillary column listed in the method. Either liquid chromatography or GC/MS spectroscopy should be used if individual quantitation of these four pairs is required.

Summary of method

77. The sample is appropriately liquid-liquid, soxhlet, or sonicatively extracted. Some nonaqueous wastes require only solvent dilution. The extract is dried, concentrated, solvent exchanged with hexane, and reconcentrated to 1 ml using a Kuderna-Danish concentrator. A portion of the extract (2 to 5 µℓ) is injected into a flame ionization equipped GS.

Equipment and operating conditions

78. The following equipment and operating conditions apply:

a. Gas chromatograph conditions.

(1) Column 1: 1.8-m by 2-mm-ID glass column packed with 3-percent OV-17 coated on 100- to 120-mesh Chromsorb W-AW-DCMS or equivalent. The column temperature is held at 100° C for 4 min followed by a 8° C/min program to 280° C and held until the analysis is complete. The nitrogen carrier gas is set to a flow rate of 40 ml/min.

(2) Column 2: 30-m by 0.25-mm-ID SE-54 fused silica capillary column. The column temperature is held at 35° C for 2 min followed by a 10° C/min temperature program to 265° C and held for 12 min. The helium carrier gas is set to a flow rate of 20 cm/sec.

(3) A sample volume of 2 to 5 μℓ is usually used.

b. Data system. A data system is preferred for the measurement of peak areas or heights and RTs from the point of injection.

Interferences and contamination

79. All reagents, glassware, solvents, reagent water, gas chromatographic carrier gas, etc., must be free of any compound(s) that would interfere with the PAH analysis above the MDL for that parameter. Extreme care must be exercised in the glassware cleaning process to avoid introducing sample cross contamination. Carry-over between analyses can be troublesome when high-level samples are followed by low-level ones. Matrix interferences can be especially difficult depending upon the nature of the sample. Activated silica gel column cleanup is useful in eliminating nonpolar interferences (e.g., aliphatic compounds) which interfere in these analyses.

Identification and quantification

80. Identification and quantification are usually accomplished by the external standard procedure. By this approach, the analyst matches the RT of the peak(s) present in the standards with peaks in the sample. Identifications based on RT should take into account any RT changes occurring during the analysis of standards analyzed before and after the samples. For example, 2 SD are used as a warning limit, and 3 SD are used as an outmost limit in the calculation of RT windows for identification.

81. Quantitation is based on area or height response of the detected parameter versus concentration derived from a 5-point calibration curve. When the external standard approach is used, it is particularly important to confirm all positive identifications on a GC column of differing polarity from the main analytical column. This will add more creditability to the identification.

Quality assurance/quality control

82. A laboratory that performs this method of analysis is required to initiate a QC program that has as a minimum the following points:

a. Each analyst must make an initial demonstration of the ability to generate acceptable data through the measurement of precision and accuracy by analyzing four separate replicates of a check sample containing all parameters of interest. These data allow the generation of control charts for each parameter against which all future data can be monitored. The resultant precision and accuracy data must fall within the guidelines of Table A34.

Table A34

Quality Control Acceptable Criteria,* Method 8100

Parameter	Test Conc. µg/ℓ	Limit for SD** µg/ℓ	Range for X,† µg/ℓ	Range P, P_s †† %
Acenaphthene	100	40.3	D-105.7‡	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1- 11.6	12-135
Benzo(a)pyrene	10	4.0	0.2- 11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8- 13.8	6-150
Benzo(g,h,i)perylene	10	2.3	D- 10.7	D-116
Benzo(k)fluoranthene	5	2.5	D- 7.0	D-159
Chrysene	10	4.2	D- 17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3- 10.0	D-110
Fluoranthene	10	3.0	2.7- 11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2- 10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4- 12.1	D-140

* Criteria based on 40 CFR Part 136 for Method 610.
** SD = standard deviation of four recovery measurements.
† X = average recovery for four recovery measurements.
†† P, P_s = percent recovery measured.
‡ D = detected; result must be greater than zero.

b. The laboratory must analyze a reagent blank, matrix spike, and matrix spike duplicate/duplicate as a minimum for each analytical batch up to 20 samples. The spike value should be in the range of 1 to 5 times the value in the samples. After the analysis of five spiked samples (same matrix type) the accuracy can be expressed in control charts as average recovery ±2 SD to monitor data quality.

c. The laboratory must routinely analyze a check standard sample containing all parameters of interest. The need for check standard sample analysis increases with the complexity of the sample matrix and the number of analytes present. If an analyte spike value falls outside the range of recoveries (from the QC chart, item b), a check standard sample must be analyzed. The concentration for the check sample concentrate is as follows: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene, 100 µg/ml each; benzo(k)fluoranthene, 5 µg/ml; and any other PAH at 10 µg/ml. The QC guidelines in Table A34 must be met.

d. A reagent water blank should be analyzed with each set of samples to verify that the entire system is free of any analytical interferences for the parameters analyzed.

e. The analyst must verify at the beginning of each shift that the established calibration curve is valid by the analysis of one or more calibration standards. The response should be within 15 percent of the original response.

f. A mid-level calibration standard should be run after each group of 10 samples to verify the initial calibration.

g. The surrogates recommended in PAH analysis are 2-fluorobiphenyl and 1-fluoronaphthalene. Each sample, blank, and spike must contain the surrogates. Once a minimum of 30 samples of the same matrix type have been analyzed, the average percent R and standard deviation of the percent recovery for each surrogate can be calculated. The method performance for the surrogates should be calculated as $R \pm 3\ SD$.

h. Any parameter result beyond the calibrated range must be diluted within range.

i. The laboratory should, on a continuing basis, analyze external QC blind samples to check method performance.